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FLAME

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FLAME

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PLATE

FIG. 14 *Facing 89*

INTRODUCTION

IDEAS about flame go back to the beginning of ideas. Their development is traced elsewhere ⁴⁰. In the small compass of this book the authors cannot attempt more than a brief survey of the present state of our knowledge.

The flame of a morsel of solid fuel, burning in air, consists of a heterogeneous mixture of gases, mutually reacting with emission of heat and light. The mixture is sustained by the diffusion into the flame of air coming from without and of vapours, distilled from the surface of the fuel, coming from within. The form of the flame is determined by a variety of circumstances, but there is always the effect of the disparity that exists between its own density and that of the air; and there is generally the effect of the motion of the dark hot gases that have burned and now rise rapidly into the air.

The simplest example is the flame of the candle, drawn upward by its own draught. There is a dark central region; this consists of the vapours of the fuel, changing chemically because of the temperature, but not burning. Then comes the yellow, luminous region where the vapour is mixed with a little entering air and burns with the precipitation of sooty particles which are incandescent not merely as a "mantle" or a wire is incandescent when heated, but also because they are largely consumed as they meet more air. There is a faintly luminous region between the two, another between the yellow zone and the air, and a third at the base, where the flame almost touches the fuel.

The flame of a fuel that is liquid may also be exempli-

fied by the flame of the candle (since it is exactly similar to the flame of a lamp), the process of distillation being a common essential to the combustion of all non-gaseous fuels ; but here the function of the wick is not only to serve as a stillhead for the fuels but also to localise the combustion and thus to keep it under control.

It will be clear, as Davy ¹ pointed out, that all flame consists in the combustion of an explosive mixture of gases ; and at this point it may be well to say something of what is meant by the word " explosive ". The explosion of a mixture of mutually reactive gases may in certain circumstances be indicated by a percussive expulsion of gas from the container, but this is no essential criterion of the phenomenon to which the word " explosion " is nowadays applied. An explosion occurs when the radiant shell passes through the mixture. The quiet burning at the mouth of a " bunsen " is no less an explosion than the burning-back to the base which is attended by a noise. It is true also, therefore, to say that an explosion occurs when the mixture passes through the radiant shell. The inner cone of the Bunsen flame is a true explosion-flame. The outer hood consists merely of the burning of fuel surpluses and end-products in the atmosphere, and it may be reduced to a negligible thickness by forcing the air-supply until the burner becomes a " blowpipe ". The inner cone of the Bunsen flame is thus a stationary explosion. Its angle fluctuates with the rate of the upward stream. When the gas-tap is gradually closed, the cone declines to a flat disc, dips inward, and passes down the tube. That is the most commonplace example of the " propagation " of flame through an explosive mixture of gases ; it is produced by the introduction of air into the distilled gas before it becomes flame. If, on the other hand, an inflammable gas is present in the atmosphere round a flame, there are further phenomena : when the content is small, there is luminous combustion in a small outer zone which is called a " cap " or " spire " ² ; as the content is made larger, the vertical dimension of this aureole

is extended until, in atmospheres which are all but explosive *per se*, it becomes a pillar of flame which tends increasingly to burn outwards and downwards. This is a "flare".

The simplest example of the "propagation" of flame through an explosive mixture of gases occurs however when ignition takes place at the centre of a rigid spherical container, every plane passing through a diameter being a plane of symmetry. The faintly luminous surface of the flame is itself a hollow sphere concentric with the container; the motion of the unignited gas outside it is uniformly centrifugal, (its own movement is uniformly centrifugal until it dims, yielding its rôle to the neighbouring outer layer) and the movement of the ignited gas within it is uniformly centripetal.³ The rigidity of the container obviates atmospheric disturbances which are not absent when the sphere is a bubble; and gravitational effects may for most purposes be entirely neglected when the period of inflammation is small. Many costly researches have been vitiated because these conditions have not been observed, and "central ignition in a sphere" is now the usual arrangement for many types of flame-analysis.

The pressure-system is dynamic, since a continuously renewed generator is continuously dissipating its power. The fall of pressure inward from the flame-surface to the centre is steeply exponential without discontinuity. The fall of pressure outward from the flame-surface to the wall, however, is preceded by an abrupt fall, since the surface of the flame, which is in most respects the acme of pliability, is in this respect an unbreakable piston-head. The fall of pressure in the unignited gas is therefore strictly comparable *mutatis mutandis* with the fall of pressure along a cylinder that is receiving a moving piston.³

Whether because the pressure at the flame-surface reaches a critical value characteristic of the mixture or because the rate of rise of pressure at the flame-surface reaches such a value, flame may in certain mixtures be

propagated at a rate comparable with the speed of sound in the hot gases or with that of the molecules themselves. This is the phenomenon of detonation. The rise of pressure in the container is otherwise unfavourable to a high rate of propagation of flame.

The distribution of temperature is less simple. It falls sharply outward from the flame-surface into the neighbouring unignited gas ; if the thermo-chemical equation were realised at the flame-surface and if there were no further irruption of heat in the interior of the flame, it would in its earliest stages fall continuously inwards also, the fall extending to the centre : that normally this does not happen is an important datum in the formulation of a theory of gaseous combustion.

The retarded completion of the energy transaction is often manifested by the emission of radiation from the ignited gas within the flame. This residual emission of energy is not fully accounted for by shifts in the chemical equilibrium that are brought about by the rising pressure ; it occurs also when no such effects are possible. The region chiefly concerned emits that visible radiation which is usually and naturally regarded as characteristic of the flame-surface (because the infra-red radiation, which is far more truly characteristic of the surface, is invisible). This visible radiation is immediately due to the quiescence of electrons towards their final orbits within their molecules. A proportion of the molecules lose electrons by collision ; it is this loss and this restoration that confer upon flame-gases certain electrical properties which will be reviewed. The radiation may be analysed by the spectrograph and assessed by the photo-cell. This examination demonstrates that the emitters from the flame-surface are not all always present in the ignited interior gas which is chemically quiescent. The emission from this gas is ascribed to the operation of the rising temperature upon the freshly produced linkages. Its appearance was noted in the case of electrolytic gas by Bunsen ⁴ ; and Frankland ⁵ showed that a continuous spectrum was produced both

by this mixture, and by the similar mixture that contains carbon monoxide instead of hydrogen.

This phenomenon may be observed also in jet-flames: Frankland⁵ produced it in the hydrogen flame by increasing the pressure; Smithells⁶ produced it more simply. He showed how the two cones of the aerated flame of Bunsen's burner might be "separated". In this invention he may be regarded as having sheathed the mixing-tube of a bunsen-burner with a longer outer jacket. In such an arrangement, an adjustment of the rate of mixture-supply will—while leaving the outer cone at the outer extremity of the jacket—cause the explosion-flame, the "inner cone", to "burn back" through the ascending mixture to the end of the mixing-tube. Now under these circumstances the "inner cone" may be swathed in an aureole⁷ somewhat less luminous. Mixtures that give this aureole at atmospheric pressure in the separator may naturally exhibit it also when the flame "burns back" or passes through the mixture at atmospheric pressure in any other experimental arrangement⁸.

In the ordinary jet-flames of carbon compounds—as of methyl alcohol, which Frankland⁵ made to burn with a bright white light—the increase of illumination under pressure is probably mostly due to an increased production of the incandescent carbonaceous solid particles to which Hooke⁹, and later Davy¹, ascribed the light of flames. The proportion that is due to these particles may also be increased by increasing the carbon content of the fuel (as in Henry's¹⁰ substitution of unsaturated hydrocarbons for methane), or by raising the temperature of the flame (as in Neilson's invention of directing two flames into a common zone of combustion). The operation of temperature is again of especial interest: that it has a share in the production of light from incandescent particles is proved by the experiments of Knapp¹¹, who fed the mixture-supply of a luminous flame with various diluents with the effect of making it non-luminous; that it has also the other

rôle, previously mentioned, is again shown by Wibel's¹² experiments—in which he made the ordinary bunsen-flame luminous by merely heating the mixing-tube—together with Heumann's¹³ corollary investigation, which demonstrated that this heating did not alter the composition of the gas-mixture supplied.

The processes of ignition provide the experimental investigator with perhaps his most difficult subject. "Ignition" refers to the extremely minute volume of gas that is first enkindled. The ignition may be due (as in the later propagation) to the proximity of the mixture's own flame, and the first increase in kinetic energy (and in consequent molecular collisions) is due almost solely to the temperature, since burned-out end-products or hot inert gas will also cause ignition. It may be due to spark or other discharge, where the first increase in kinetic energy (and in consequent collisions of molecules and ions) is induced electrically. It may be due to a hot surface, where the preparation is not altogether independent of the actual orientation of the adsorbed molecules. It may be due to adiabatic compression, which includes too many possibilities to be free from doubt as to each contributory item. The processes of flameless combustion and of the "cool flames" are studied with much less difficulty, though the difficulty remains considerable.

An explosive mixture that by a small alteration in constitution or condition may be rendered non-ignitable is called a "limit-mixture", and the term is most commonly used of a critical mixture of the fuel with air. The speed at which flame will pass through such a mixture is comparatively very slow.

The ignitibility of a mixture is usually expressed by reference to the method of ignition. When, for example, an electric spark is employed, the minimum sparking current is such a measure^{14, 15, 16}. When the explosive mixture is raised to a given temperature, the "lag on ignition", the time taken for flame to appear, is a measure of the ignitibility of the mixture. The igni-

tibility increases as the conditions alter in a sense favourable to a greater rate of chemical reaction. The "dilution limits of inflammability" have a very definite technical value when they refer to air. The chemical reagent supplied by air is oxygen, the nitrogen acting mostly as a moderator of the reaction. It is not, however, a simple diluent; and it is customary in research to avoid the difficulty inherent in this fact by the use of argon or helium when simple dilution is all that is required. The encouragement of reaction by such bodies as nitrogen peroxide, and the inhibition of reaction by such bodies as iodine, is a branch of research in itself.

The speed of propagation of flame in an explosive mixture is a fundamental constant, and it must not be confused with the rate at which the flame moves under some particular experimental conditions; for these affect the motion of the medium through which the flame is moving. When we leave the sphere with central ignition, we admit a number of new considerations which will be examined and explained. When the container is tubular and open and ignition occurs at the vent, we have the conditions adopted for study by very many flame-investigators, and the uniform movement of the flame into the container has provided many data useful in formulating generalisations on the relative explosibilities of fuels.

CHAPTER I

WHEN a flame is started in the interior of a container, it grows at first in every direction at the same rate. If the source of ignition is a point, the flame is a sphere. As it grows, two changes may occur ; and in these two respects the flame behaves for a time exactly as if it were an unbreakable luminous bubble, blown from within. (This analogy yields still longer service if we allow for a growth of the flame that is roughly uniform and normal at every point on its surface.) There may be a change in its position, since it must move toward a position such that the resistance to its expansion is everywhere equal ; and there may be a change in its shape for the same reason. The only condition under which there is no change in position is when ignition occurs at the mass-centre of a gas-space that is compact and geometrically simple. The only condition under which there is no change either in position or in shape is Central Ignition in a Sphere. It is the lie of the wall about the flame that governs both its shape and its position ³.

Change in Position

During the initial, spherical, growth of the flame, its expansion displaces the neighbouring unburned gas, and this in turn displaces gas that is further distant from the flame. The amount of displacement decreases with the distance from the flame, because every parcel of displaced gas accepts a small compression. This compression is highest next the flame-surface ; and it falls to zero at a distant spherical surface in the unburned

gas. The radius of this rapidly receding outer spherical surface increases at a speed that is equal to the speed of sound in the unburned gas. This surface is the outermost limit of the cushion of gas that fends the flame from external obstacles and resistances. It is the end of a pressure-gradient that falls outward from the flame-surface uniformly in every direction. It encloses all the gas in which there is a flow or displacement due to the expansion of the flame. This flow is outward from the flame-surface in every direction, and the rate of this flow at any point is a function of the pressure-gradient at that point. As soon as this spherical limit of acoustic disturbance reaches the wall of the container, the pressure tends to mount there, and fending begins, the pressure-gradient along this radius becoming stationary and the radius itself increasing as the flame expands preferentially in other directions. Thus in any compact gas-space the most noticeable result is that the lie of the wall, the external resistance to the outward flow from the flame-surface, causes a centring of the flame in the cavity³.

Change in Shape

For the same reasons (since the flame-surface, though unbreakable, is exquisitely pliable), as it smoothly changes its position there is a smooth change in its shape. The flame does not only move toward the centre of the container: it also accommodates itself to the shape of the containing cavity. Since gas must always be quiescent, in the sense that there must always be flow towards a uniform level of pressure, the general flow in the gas-space is dictated by the maintenance of two isobars. There is an isobar at the wall of the container, or a rectifying flow that tends to establish it; and there is an isobar at the flame-surface. The isobar at the wall is stationary; the isobar at the flame-surface is mobile. There is a flow from one to the other that compounds with the flow which is centring the pressure-source (the flame) in the container. The flame-surface

burns into this flow and is thus extended preferentially in the direction of greatest room ³.

Change in Area

Another way of stating this is to say that the isobars in the unburned gas tend to every shape intermediate between that of the flame-surface and that of the bounding wall, and that the flame-surface tends to lie successively upon these shapes. If for any reason the isobars are disturbed, and thus increased in area, the flame-surface in due course registers this disturbance. The disturbance may be produced from the exterior by the force of a jet, or a fan may be spun in the gas-space ¹⁷⁻²¹; or there may be some local fall of pressure due to local cooling or to the development of a leak. Just as the flame in a container that is shaped like a cone will taper towards the apex, so a flame in a gas-space open to the atmosphere will taper toward the leak or orifice. Similarly, a flame in one compartment of a chambered gas-space moves toward the communicating orifice; and a flame in a chamber of a gallery that is not uniform in structure is extended towards the vents, symmetrically only if the ventage is symmetrical. When the flame has passed through such an orifice or tunnel or restricted channel, it appears on the other side as a long tongue having a very low ratio of volume to surface-area. Here it may increase its area with consequently high rapidity; or, on the other hand, it may be pulled right back into the first chamber by some collapse of the pressure within the flame-gases ³.

Such a collapse is brought about when a large tract of the flame-surface comes into contact with the wall of the container. For this has two results, both tending to the collapse of pressure: first, there is the local cessation of pressure-generation; and secondly, there is the creation of an actual drain of energy (by cooling) over the region of contact. Thus, in general, it may be said that a flame that starts at the wall, or at some later stage makes contact with the wall, is held to it by the

same forces that hold a submerged bubble of vapour to the wall of a beaker containing a liquid that is about to boil ³.

Another cause of collapse of pressure in the flame-gases is seen in experimental techniques wherein some of the internal gas is drawn off through a hollow probe into a vacuum. Finally, pressure within the flame may be lost if a leak or burst is developed in the region of cooling contact. In any event, the position of the flame-surface is affected by every volume-change or pressure-change as between the ignited gas and the unignited gas. If a leak or burst is developed outside the flame, the movement of the flame towards it is much swifter than if the orifice had been operative throughout the whole of the flame-period; and the degree of turbulence is heightened accordingly ³.

Rise of Pressure

When ignition is central in a sphere the internal pressure mounts, as more and more gas is burned, until as the last spherical layer is inflamed, it reaches the maximum. This maximum pressure, P_m , has a value higher than can be attained under any other condition; for there is no other condition under which all the gas in the container can be burned without a severe local loss of energy due to cooling. This maximum represents the translation into expansion, and thence into pressure, of all the heat liberated during the flame-period that is not dissipated in radiation and in conduction-losses. (There can be no loss by convection: the flame is the gas "conveyed".) ³

Although the combustion of the same gas-mixture in a differently shaped gas-space would proceed to a maximum pressure of lower value, there are portions of the flame-period during which the rate of rise of pressure will be greater. For comparative periods prior to contact between the flame and wall, the rate of rise of pressure is at a minimum when the container is spherical and ignition is central. The extension of the flame-

surface towards regions of lowest pressure increases the rate, because at any selected point in the rise of pressure the pressure-generation is proportional to the surface-area of the flame. Similarly, a local fall of pressure due to a local release of unburned gas greatly increases the rate because of the responsive expansion of the flame towards the vent. Even the loss of pressure by contact of burned gases with the wall may cause an increase in the area of the flame-surface, so that this loss may still diminish the nett figure of maximum pressure reached rather than the nett rate of rise of pressure ³.

Clerk ¹⁷ showed, however, that a maximum pressure nearly as great as that associated with central ignition in a sphere can be produced (with very rapid rate of rise) in a non-spherical gas-space. This occurs when the igniting agent is an antecedent explosion in a small auxiliary compartment; for a shaft of gas is thrown thence very abruptly into the major container, and an atomised spray of flame, consisting of innumerable independent points of ignition, follows upon it. Here again is the principle of the chambered gas-space which, as Beyling ¹⁵ was to show later, must be eschewed if rapid rise of pressure is to be avoided. A similar result in turbulence (which is a crumpling of the isobars, and consequently of the flame-surface) is obtained by the entrance of a shaft of gas alone, as was pointed out by Schlösing and Demondésir ¹⁸, who shortened the time of total inflammation of a quantity of gas-mixture by spirting a jet into it. This is the principle of the carburetter. In the cylinder of the internal combustion engine, the flame starts in a wind-storm; the charge enters on the heels of the piston in a misty jet at the speed, as Clerk put it, of an express-train. The charge is already turbulent when ignition occurs, and its propagation is turbulent. Such turbulence has often been imitated in experimental techniques by the use of a spinning fan ¹⁹⁻²¹.

The maximum pressure attained in a vented container varies with the relation between the form and

area of the vent and the volume of the container. The importance of the lie of the wall about the flame has somewhat diminished. The flame behaves as if it were the flame of the antecedent explosion in Clerk's experiment, with the atmosphere as the major container. Yet the position of the ignition has its importance: ignition at the wall opposite the vent means that the flame sweeps the container clear of unburned gas; ignition at the vent means that the flame burns into the container against a contrary motion; intermediate ignitions involve a sailing of the flame to the vent, followed by an inward burning against the gas-flow. Every additional intricacy of flow means an increase in area of the flame-surface, and thence an increase in rate of rise of pressure with a consequent development in the gas-flow. There is thus a culminating voiding of the cavity into the atmosphere; this is percussive, and is what is intended in non-technical language by the word "explosion".

If the ventage is not opened until some time after ignition, these effects vary according to the pressure that has been attained and the development of the flame which till now has grown in a closed gas-space. In experimental work, the ventage may be the rupture of a soap-film, or the break-down of inertia of gas-flow in a capillary, or the blowing of adhesive tape away from an orifice that it closes, or the smashing of a glass lamina; but ventage is most satisfactorily timed by some kind of accurately controllable automatic mechanism³.

The Gas-Flow in a Spherical Container with Central Ignition

The pressure-gradient in the kindled gas falls rapidly and smoothly from the flame-surface inwards to a value of the same order as the mean pressure in the container. If we take a section at a diameter, the flame-surface is a "ridge of high pressure". The height of this ridge, and the sheerness of the inward fall, will be modified

by any delay in the emission of energy from the kindled gas. This inward flow within the flame probably sustains the tendency of the surface to remain a sphere, even when ignition is not central in a spherical gas-space; it has no other important effect. The shedding of pressure in this inward flow from the watershed ridge is the same share of the total pressure that is being generated at the flame-surface as the volume of the flame is of the total volume of the gas-space.

The flow in the unburned gas falls from a value at the ridge along a pressure-gradient that is the same as if the flame-surface were the moving head of a piston. That the pressure (as well as the temperature and density and chemical constitution) is abruptly changed at the flame-surface is evident, if only from the consideration that the pressure just outside it is continuously rising while the pressure just inside it is continuously falling. The rate of flow in the unburned gas at any point appears to vary inversely as its distance from the flame-surface³.

Gas-Flow under Asymmetrical Conditions

These conclusions require little alteration for the conditions where ignition is central in any compact gas-space. Where ignition is not central (and not at the wall) there is the slight asymmetry of flow that pushes the flame toward a central position. Where ignition is at the wall, the inward flow within the flame is increased to compensate the cooling of the kindled gases that have made contact with the wall; less energy is available to move the residual flame-surface, and the nett "propagation" is slower. The maximum pressure attained, moreover, has a lower value, as is shown by fig 1 in which ignition at the centre of a sphere is compared with ignition at various other points.

Pressure-meets and Planes of Stillness

When two flames grow symmetrically in the same container, there is between them in the unburned gas a

surface separating the two outward flows. On both sides of this surface the gas is flowing towards it, but there is no motion at the surface. This "pressure-meet", a word coined on the analogy of watermeet, is a plane of stillness and is undisturbed throughout the explosion. If the flames are not symmetrically

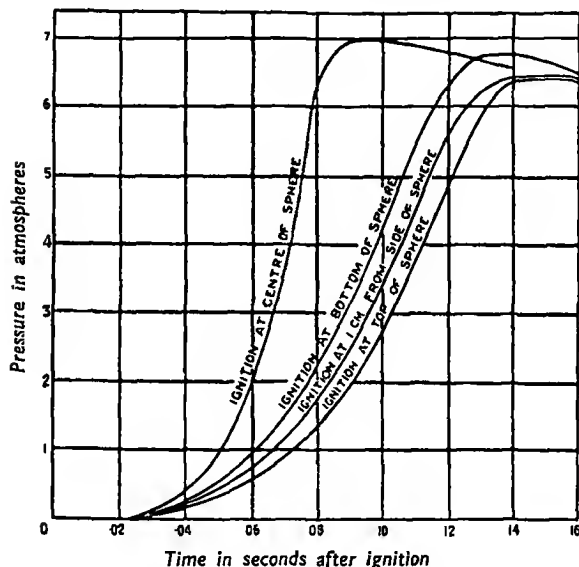


FIG. 1

placed, this surface moves undisturbed towards a position of symmetry; but in either event each flame behaves at any moment as if the rigid partition which we have called a pressure-meet were a solid wall. If, for example, we employ a tube having a length which is an integral multiple of its diameter, we may regard it as a series of square cylinders, sealed rim to rim; and we may start a flame at the same moment at the centre of each.

All the flames will behave exactly as if the square cylinders were mutually separated by solid partitions. This has enabled Ellis and Morgan³⁴ to examine the temperature-gradients in nearly spherical flames without involving the curvature of the container in their calculations. They employed quintuplet flames. (See fig. 3 in refce. 34, fig. VIII 3 in refce. 40, or fig. 23 in refce. 7.)

On the other hand, if in such a composite tube one flame is started before the others, the younger flames will move at first in the flow that it has set up as "straws" or "marker-flames" registering the speed of this flow; but, as their size becomes significant, pressure-meets will be established, and the behaviour of each flame will be regulated at any instant by the size and shape of the gas-region that is bounded by the wall of the tube and the then position of the nearest pressure-meets³.

Convection and Gravitation

If the source of ignition is a gradually heated surface, such as a wire bearing an electric current, convection is set up in the gas before the flame is started; and there is a consequent compounding of this factor with those already described. When the explosive gas-mixture has a very high thermal conductivity, there is a characteristic fraying or pitting of the flame-surface. Apart from these two instances, convection is limited to the post-flame hot gases; during the flame-period, while there is convection within the flame, there can be no convection, properly so called, in the unburned gas around it. This gas does of course, however, suffer the motion consequent on the expansion and upward translation of the flame. Indeed, the effect of gravitation is always apparent, except in the propagation of flame from the centre of a small spherical gas-space containing a mixture of short flame-period. When the movement of flame is to be predicted, an upward vector must always be compounded with the other forces considered. Flame tends to slide upward past the mixture into which it is burning, just as air-banks slide past each

other in the atmosphere. Any propagation, for example, that is initially horizontal soon becomes canted. The apex of the coned form that is adopted by the flame-surface after the "arrest" in a closed tube (see pp. 40, 86) falls along a parabola.

The apparent absence of gravitational effect upon a flame that is started at the centre of a sphere containing a mixture of short flame-period is partly that the acceleration starts from zero and has little time to develop, and partly that the denser surrounding gas, which would mould the flame, is quickly merged with it and has no reinforcement from the atmosphere; for when a flame is thus started, even in the fastest mixtures, if only they are contained in a bubble, the moulding of the shape of the flame is clearly seen. This change of shape and position is best observed, however, in a closed spherical gas-space containing a mixture that is only feebly inflammable. If ignition takes place anywhere on the vertical diameter, the flame rises through the mixture, taking the shape to be expected of any light, pliable, submerged body. Thus its vertical chords tend to equality, and a recess is developed at the base. As the flame develops a boring action, this recess becomes a sharply defined cusp. This rise of the entire shell of flame takes place even when the ignition is at the base of the sphere, the adhesive tendency being entirely overcome by the gravitational one.

When the crown of the flame reaches the roof of the sphere, an extensive area of cooling is formed, the pressure in the sphere falls, and the unburned gas beneath the cusp is greatly expanded. Then this vortex-shaped flame-surface burns slowly downwards in the spinning gas to the base of the sphere.

In the weakest mixtures, the recess is not a cusp but develops a symmetrical vase-form. Disturbed, the flat disc that has replaced the point of the cusp may become an oscillating protuberance.

When ignition is not on the vertical diameter, a vector representing the centripetal action of the gas-flow is

introduced. This applies also to experiments in gas-spaces that are not spheres.

In mixtures of intermediate inflammability, the effects are a slight rise of the mass-centre and a flattening of the flame-base. In a vented vessel, flame in a weakly inflammable mixture sails to the vent and lodges there; where the mixture is a "rich" one, a flame of the bunsen type is then constituted, with an inner cone that tends to burn back into the vessel and will do so if the mixture is not too rich to admit the propagation "per se" of the flame³.

Rotation

The apex of the coned flame-surface, that falls along a parabola under other conditions, travels in a thin helix when the tube is vertical; and it would appear that this boring movement is the inevitable method of the expansion of one body of gas through another. In detonation, the path of the flame is helical^{3, 79}.

Detonation. The Pressure at the Flame-Surface

The speculation of Mallard and Le Chatelier¹⁵⁶ as to the initiation of this phenomenon has been generally adopted. Nernst²², for example, writes: "First we have the condition of slow combustion, heat being conveyed by conduction at adjacent layers and there following a speed of propagation of a few metres per second. But owing to the high increase of pressure that accompanies the combustion, the speed of motion of the flame must continually increase. As soon as the compression in the still unburned layers becomes so great that spontaneous ignition results, the now much more pronounced compression-waves must be propagated with very great velocity, and we have the spontaneous development of a detonation-wave." This picture has not been challenged. If we adopt it, we must imagine that in a series of mixtures that detonate, the height of the ridge of pressure in the flame-front depends on the intensity of the chemical reaction there. When the

mixture is electrolytic gas, this pressure is of the order of twenty atmospheres ^{23, 24}. We must further imagine that in a series of mixtures that do not detonate, the pressure in the flame-front varies from a small quantity (with very weakly inflammable mixtures) to a high value (with mixtures that all but detonate). In the initiation of detonation, this pressure in the flame-front must reach a critical value characteristic of the mixture.

Flame Temperatures

When a mixture burns at atmospheric pressure, the temperature of the surface of the flame may be assessed by colouring it with sodium vapour and balancing the brilliancy of the D doublet against the continuous spectrum of a tungsten strip ²⁵⁻³¹. Attempts have also been made to apply this method to the flame-surface of an explosion in an enclosure. As to the gas behind the flame, its temperature has been assessed by changes in the resistance of current-bearing wires ^{32, 33}, by the response in current of thermo-electric junctions ⁷, and by measurements of its refraction of a line-shadow ^{28, 34}. In an enclosure, the temperature of the gas usually mounts from the flame-surface towards the interior of the flame ³²⁻³³; and this is not merely an effect of the compression of the burnt gases: it occurs before appreciable compression can take place.

Measurement of Pressure

The earliest attempts to measure the pressures produced in gaseous explosions were probably those of Cecil ³⁶ (1820), who made explosions rupture strings of known breaking-tension, and of Bunsen ⁴, who measured the mass that an explosion would lift against gravity. The object of such investigations was usually the calculation of explosion-temperatures.

In 1861 Hirn ³⁷ published explosion-pressures that had been obtained with a Bourdon spring manometer. Twenty years later, Berthelot and Vieille ³⁸ used a light piston working against a spring in a tube, which was

attached to the iron explosion bomb; and at about the same time Mallard and Le Chatelier³⁹ employed a Bourdon gauge.

Dugald Clerk¹⁷ (1886) was the first to obtain a record of the development of pressure during the passage of flame through an explosive mixture. It was odographic. He used a Richards indicator, replacing the reciprocating drum by a revolving one. This carried smoked paper to record the movement of a scribing style. The pressure of the explosion acted on the indicator piston, and the attached pencil traced on the drum a "pressure-time record", which showed the rise of pressure during the explosion and the progressive loss of pressure on subsequent cooling.

The most notable types of pressure-recorders used in recent years are those in which the explosion-pressure "does work" against a very strong spring or against a metal diaphragm, the resultant small movements being magnified by optical methods. The best-known example of the first of these types is the Petavel manometer; and diaphragm manometers have been used by Fenning⁴¹, Morgan⁴¹ and others. The inertia and lack of critical damping of nearly all these manometers tend to invalidate the pressure-records obtained, because of oscillations in the moving parts of the manometers themselves; especially is this so with the faster-burning mixtures, or with a vibratory propagation of flame.

An electrical recording manometer of low inertia and high natural frequency has been described by Allsop and Lloyd⁴²; and this has been successfully used for recording very rapidly developed explosion-pressures. A diaphragm unit receives the pressure, and the small movements of the diaphragm are detected through the consequent changes in the electrical capacity of the system. These produce corresponding changes in the current of a valve voltmeter circuit, and can thus be recorded on an oscillograph.

Many investigators have sought to utilise explosion-pressures for the determination of specific heats. The

method was never satisfactory and it is now definitely superseded by the spectroscopic method of Nernst.

For the measurement of pressure-changes in the vicinity of the head of a detonation-wave, or of a shock-wave, Robinson ²³ has developed a method, used—following Thomson's suggestion ²³—by Keys ²³, that employs the piezo-electric properties of certain crystalline substances. In particular he has used a slab of tourmaline suitably cut with respect to its crystallographic axes. The relation between the applied force and the quantity of electricity that is generated is linear, and with tourmaline is 5.4×10^{-8} e.s.u. per dyne. This "piezo-electric gauge" has no moving parts and there is no inertia or lag. It develops immediately the extremely minute high-voltage charge due to the operative pressure. The voltage is recorded on a cathode-ray oscillograph—the only type of oscillograph that is not debarred, by reason of the inertia of its moving element, from faithfully following the voltage variations of the gauge. The somewhat earlier method of Campbell ²⁴, applicable to the detonation-wave alone, depended on the rupture of laminae of metallic foil stretched across the entire cross-section of the containing tube.

CHAPTER II

The Registration of the Movement of Flame

CERTAIN early methods of recording the movement of flame-surfaces are now of only historical interest. Such are the method of Bunsen ⁴, who balanced the outward flow of an ignited jet of explosive mixture against the inward movement of the flame-surface through the mixture; the method of Fonséca ⁴³, who forced the jet at high speed from its orifice and determined his result from the dark gap between; the method of Schlösing and Demondésir ¹⁸, who employed a stop-watch to record the point-to-point motion of a flame-surface along a tube; and the Pneumatic Method of the Marey drums ⁴⁴.

Methods now usually employed only upon special problems where photography is out of the question have been based upon the rupture of L.T. electrical circuits at metal strips placed in the path of the flame ⁴⁵⁻⁴⁸, the completion of H.T. electrical circuits by the discharge across the flame upon its arrival at selected points ⁴⁹, and the current-change in electrical circuits ³³ by the increased resistance of metal strips in the path of the flame when its surface reached them.

The bases of the photographic registration of the motion of light-emitting bodies against a dark background have been very fully explained by Marey ⁴⁴. It was he who in 1877 combined with these the odographic principle of Poncelet and Morin ⁴⁴ into a contrivance by which a continuous image of a luminous trajectory was projected on to a moving surface that was photographically sensitive. In odography, motion in

one direction is scribed upon a surface moving in another direction; when the scribing pencil is a ray, the method may be called odophotography. This method was introduced into flame-research by Mallard and Le Chatelier ⁵⁰, and it has since been habitually employed by their successors. We owe to Wheatstone ⁵¹ the use of the rotating mirror employed in the flame-researches of v. Öttingen and v. Gernet ⁵², but these authors themselves appear to have originated the idea of governing the ignition of the explosive mixture by the motion of the mirror. It is by large increases in the speed of the relative motion of mirror and sensitised surface that the odophotography of flame has been carried to its highest pitch of delicacy and beauty as in the work of Fraser ⁵³ and in that of Payman and Woodhead ⁵⁴.

It was probably Bunsen ⁴ who first employed a slotted disc for the timed visual observation of the combustion-process; but it is again Marey ⁴⁴ who used it in the timed intermittent pictorial photography of luminous objects, using a pair of lenses so that the photographs obtained upon the stationary plate might be either single or serial, and either alternate or stereoscopically paired. This method was introduced into flame-research by Ellis and Robinson ³, who incorporated with it the idea of making the disc itself the controller of the ignition (as well as of other electro-magnetically controlled operations taking place during the experiment) in such a way as to register not only the interval between successive snapshots but also the interval by which each snapshot (or other operation) followed the moment of ignition.

This snapshot method is in many ways more convenient than the still earlier invention of Janssen ⁴⁴, who in his "astronomical revolver" rotated not the shutter but the plate itself; and it is less expensive than the method of Muybridge ⁴⁴, who used massed batteries of electro-magnetically controlled cameras. These snapshot devices, which were the immediate antecedents of the cinematograph, have not as yet in flame-research been superseded by cinematography.

The method of Spark Photography, developed by Savart, by Boys, by Töpler and by Dvorak ⁵⁵, can be applied to flame-research in two ways. Both depend upon the fact that a ray of light that is passing through a gas, or through a mixture of gases, is deflected by differences of density. The photographic material does not receive focussed light from the flame of the explosion, but is irradiated by a beam of light across which the flame passes, giving a kind of shadow. The simple shadow method of Dvorak has been applied to the photography of flames and of pressure-waves by Payman and Robinson and also by White ⁵⁶. The Schlieren method of Töpler has been similarly adapted by Payman and Shepherd ⁵⁷. Töpler's principle has been applied in the quasi-cinematography (the movement of the film being continuous) of flames in weakly explosive mixtures of hydrogen and air by Terada and Yumoto ⁵⁸. The Dvorak principle has been combined with the method of direct snapshot photography in the study of similar flames by Guénault ⁵⁹.

The Fundamental Speed of Flame

If experimental conditions remain unchanged, ignition must communicate itself to successive layers of the mixture at a constant rate, and the motion of the continuously renewed luminous shell will be uniform. The conditions that must not be changed are the temperature, the pressure, the area of the shell and the flow of gas near the shell. Then the motion of the shell through the mixture is the symptom of the continuous repetition of an unaltered process, and its rate is in a constant ratio to the "fundamental speed of flame" in the mixture. For explosive mixtures that can be burned at a jet as a regular cone, Gouy ⁶⁰ has shown that this value may be determined from the formula

$$V = v \cdot \sin \alpha$$

where V = the rate of translation of the conical shell, normal to its surface and relative to the mixture,

v = the speed of the flowing mixture, which strikes the surface of the cone at an angle,

α (the "angle of the cone").

and where, moreover,

$V = \frac{\text{the speed of the flowing mixture}}{\text{the area of the conical shell}}.$

Numerous investigators have sought to adapt and embellish this method, but it must necessarily remain inferior to any other that is free from its inherent limitations; for example, the geometrical imperfection of the cone and the impossibility of avoiding the entry, at its base, of some of the external atmosphere. In the method of Coward and Hartwell⁶¹ these flaws are eliminated, and the method has the further outstanding advantage that, by varying the experimental conditions, flame-surfaces of various areas may be made to pass through mixtures of the same constitution. In this method, a column of gas contained within a cylindrical tube is ignited at the open end. The septum of luminous shell, as it is continuously renewed, moves inward through the mixture; and it is photographed intermittently at regular intervals. So long as the shell retains a constant shape and area during a defined period of a given experiment, any change in the conditions prescribed above is indubitably negligible. Then the "fundamental speed of flame" in the mixture is obtained as before from the formula

$V = \frac{\text{the volume of gas burned per second}}{\text{the area of the shell}}.$

The tube may be supported in any position whatever, and it may be of any practicable diameter; for though a change, either in diameter or in orientation, will affect both the numerator and the denominator of this ratio, it does not affect the ratio itself.

Lewis and von Elbe⁶² have developed a method for determining the "true speed" of flame, relative to the moving unburned gas at any point in a closed sphere. Their determinations depend on analyses of time-

pressure records of explosions. The basis of the calculations is the establishment of the relation between the amount of gas burned up to a certain time and the pressure established at that time. They have employed the work and equations of Maché³⁵ to deduce that the speed of flame,

$$S = \frac{dr_i}{dt} \left(\frac{r_i}{r_b} \right)^2 \frac{T_u}{T_i} \frac{P_i}{P}$$

where r_i = "radius of the burned phase when no expansion occurs."

r_b = radius of sphere containing the expanded burned gas.

T_u = temperature of the "unburned phase".

T_i = initial temperature of gas.

P_i = initial pressure of gas.

P = pressure of burned gas.

Speed Determinants

Three formulae have been proposed as bases for discussion and experiment. The first is that of Mallard⁶³ (1875):

$$V = \frac{T - t}{t - \theta} \cdot \alpha \cdot \sqrt{\frac{2L}{r \cdot y}}$$

where V is the speed

θ initial temp. (abs.)

t ignition temp. (abs.)

T temp. abs. of kindled gases

α a constant for the mixture

L thermal conductivity of the mixture

$r \cdot y$ constants of the tube.

In the second, that of Mallard and Le Chatelier⁶⁴ (1883), the terms relative to the tube are discarded; since the material of the tube (giving y) is no longer regarded as having importance, and since the authors believe that if a tube of sufficiently great radius is employed, r can be omitted. The speed is made proportional to the conductivity instead of to its square root, and the term c ("the mean specific heat of the

kindled gas between 0° and T ") is inserted. Then, if k is a numerical constant, the speed may be given by

$$V = k \cdot \frac{L}{c} \cdot \frac{T - t}{t - \theta}.$$

In the third equation, that of Daniell ⁶⁵ (1930), the whole expression is put under the root-sign and three new terms appear.

f is "the rate of reaction, that is, the reciprocal of the time in which the reaction is completed"

ρ_0 is the initial density of the mixture

θ_3 is a harmonic mean temperature which is probably nearer to T than to t

c is definitely C_p . The equation is

$$V = \sqrt{\frac{T - \theta}{t - \theta} \cdot \frac{L f}{\theta_3 c \rho_0}}.$$

Discussion and experiment have largely been limited to the second of these. In none of the equations can we substitute values and thereby calculate the speed of flame through a mixture; but large support for the soundness of the second equation may be found in the fact that during fifty years of research, experience has shown the truth of certain contributory factors and of certain deduced corollaries. The term $\frac{T - t}{t - \theta}$ finds strong support in the results of Mason and Wheeler ⁶⁶. They conclude that in mixtures of the same thermal conductivity the speed is proportional to the numerator of this term and inversely proportional to the denominator. The equation may also be examined in the light of considerations relating to Reaction Velocity, Calorific Value and Thermal Conductivity.

Reaction Velocity

This is a term which Chemistry has accustomed us to apply to the progress of homogeneous reaction in an intimate mixture, and some caution is necessary in its use relative to the zone of reaction that moves through

such a mixture when the problem is that of flame. It will depend on the frequency of collision, that is, on the temperature and pressure; on the energy of activation; and on the numerator of the mass action expression, that is on the product of the concentrations of the reacting bodies: and this last factor is perhaps the most important as being nearly akin—if we except the energy of activation—to the origin of the others. On this account, Payman⁶⁷ has argued that in a series of mixtures of oxygen with an inflammable gas the speed of flame will be greatest in the balanced mixture and that any excess or defect of oxygen will decrease the speed. The truth of this contention has been proved experimentally in two types of propagation; it is true when flame moves along an open tube at a constant speed towards the closed end, the pressure and temperature being constant, and it is also true when flame moves from the centre of a sphere (with the same development in all directions) towards the wall, the temperature and pressure rising.

The reaction velocity therefore, as would indeed be supposed from the considerations advanced in the opening paragraphs of this chapter, appears to be the over-riding determinant factor governing the speed of flame⁶⁸.

Calorific Value

In the comparison of series of similar mixtures, the equation yields various deductions which experiment confirms. Since the rise in temperature is equal to the result of dividing Q , the liberated heat, by c , the specific heat of the burning gases, or $T - t = \frac{Q}{c}$, then we may write the equation

$$V = \frac{k.L.Q}{c^2.(t - \theta)} - p$$

p being a speed-term which should be inserted in any equation to express the fact that there are mixtures

where V is zero, although the other factors are all positive. Then, in such a series as $2\text{CO} + \text{O}_2 + m.\text{N}_2$, where differences in the amount of nitrogen make large differences in Q but small differences in L , c and $(t - \theta)$, we may write

$$V = f.Q - b \text{ where } f \text{ and } b \text{ are constants.}$$

This has been proved experimentally in two types of propagation; it is true when the mixture is ignited at the centre of a sphere, and it is true when the mixture is ignited in a tube and the measurement refers to the movement of the flame during the period before cooling contact with the wall takes place⁶⁹.

Thermal Conductivity

If, on the contrary, Q is kept constant, the equation reduces to

$$V = \frac{d.L}{c^2} - a \text{ where } d \text{ and } a \text{ are constants.}$$

In view of the doubt as to the value of c , it is more satisfactory to avoid great changes in specific heat.

Then we may write

$$V = d.L - a,$$

that is, the velocity is a linear function of the thermal conductivity. That this can be true for extensive series of mixtures has been shown by firing a number of suitable media prepared by adding nitrogen to basic mixtures of the constitution $x.C + y.E$, where C stands for the balanced mixture of oxygen and carbon disulphide, and E is electrolytic gas. The choice was indicated by the low conductivity of carbon disulphide and the extremely high conductivity of hydrogen. Five series of such mixtures were prepared, Q being constant in each. In all five sets of results, it was found that

$$V = d.L - a. \text{ }^{69}$$

That this is not universally true, however, is demonstrated by the results of Coward and Jones⁶⁸ with mixtures where the diluent gases are argon and helium.

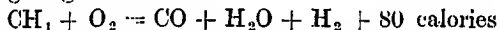
Increased Initial Temperature and Pressure

If the initial temperature of the mixture is raised before firing it, then the term $t - \theta$ is diminished and the speed of flame is increased. This increase masks the decline in Q due to the rarefaction of the gas before ignition. The result has been demonstrated in all the three types of experimental treatment that have been mentioned ^{21, 70}. If rarefaction is prevented, the consequent rise in pressure may be presumed antagonistic to increase in speed, though it will generally be masked by the effect of the increased temperature, since it has been shown that other things being equal, the pressure corresponding to the highest speed of flame is, for some unknown reason, in the neighbourhood of one atmosphere ²¹.

Displacement of the Maximum Speed

In a series of mixtures of a fuel with $x.R + y.O_2$ where R is any inert gas and the proportion of x to y is constant, Q must increase as the proportion of fuel increases, until we come to a mixture where there is exactly enough oxygen to burn the fuel completely; thus the balanced mixture of methane and air would burn completely to carbon dioxide and water without leaving any residue, either of methane or of oxygen. At first sight, it might appear that any further increase in the fuel content would waste available heat in bringing "cold" methane molecules to the temperature T without burning them; and that the surplus methane would act as the nitrogen does on the whole, that is as a diluent or cooler. On this view, however, though Q would now diminish, L increases; for the thermal conductivity of methane is higher than that of air. The speed of the flame also continues to increase, and —although as we add more and more methane we come to a point where the speed of the flame begins to diminish —the mixture in which the speed of flame is greatest contains more methane than can be burned to carbon dioxide and water.

This displacement of the maximum is general and occurs also in series of mixtures where the thermal conductivity of the fuel is less than that of air ^{63, 67}. The effect of L is almost negligible in this matter as compared with that of Q , if we define Q as the heat liberated in the chemical reaction that is taking place in the flame-front. The mixture exhibiting maximum speed must be nearly the mixture in which Q , as so defined, is at a maximum. For example, when the fuel is carbon monoxide, the balanced mixture cannot complete the combustion to carbon dioxide in the flame-surface; a more complete combustion is attained with an excess of carbon monoxide; when methane is the fuel, the flame-surface is the arena of very few triple collisions of two oxygens with one methane as compared with an enormous number of bi-molecular collisions of the type giving the reaction



half the oxygen being inactive in the flame-front, so that the addition of methane to the mixture will increase the production of heat in the flame-front and raise the speed of the flame.

These results also have been demonstrated in all the three types of experimental treatment that have been mentioned.

The Uniform Movement

It will now be well to speak briefly of the three experimental treatments which have been mentioned. In the phase of propagation that Mallard and Le Chatelier called *Le Mouvement Uniforme*, a septum of flame surface may move inward from the open end of a tube for some distance at a constant speed; and if the diameter and the orientation of the tube are standardised many useful results and theorems may, as we have seen, be based upon measurements of the displacement of the luminous septum or shell relative to the tube itself. They exact a careful technique, which has been standardised by Mason and Wheeler ⁷¹, since any dis-

turbance at the mouth of the tube may be continued throughout the propagation of the flame-shell by distortions of its shape that necessarily alter its area. When, for example, the mixture contains an excess of fuel, the gases expelled from the mouth of the tube will burn there as a jet, or "outer cone", in the atmosphere; and Mallard⁶³ expressly excluded such mixtures from certain of his generalisations. An adventitious disturbance at ignition may be equally effective in causing a change in the propagation of the flame; the shell may recreate itself steadily, it may move forward with a scooping or boring motion, or it may develop a surface that is crenellated. Thus, of a series of results of differing value for the same mixture, the value required is not the average but the least: this value corresponds to a shell of minimum area and to a gas-flow of minimum disturbance⁷².

A certain flow of gas is clearly inevitable. The flame-shell has three aspects: it is the unbreakable boundary between the kindled gas and the gas about to be consumed, so that it registers any local gas-flow; it is the source of this gas-flow which is due to its local expansion; and it is a pressure which, at the axis of the tube, presses equally in two directions, backward upon the atmosphere and forward upon the column of unburned gas. In addition, therefore, to the lift of the hot gases, there is a forward flow at the axis of the tube; and there is a backward flow near the wall, where the shell itself is a zone in the gases that are flowing outward; for the unburned gas flowing outward does not escape ignition as it bends the flame-shell back, becomes in its turn part of the flame-shell, and, having in its turn expanded, passes out of the tube. It will be noted that the column of unburned gas is at a pressure slightly higher than that of the atmosphere; but for all except aerodynamical purposes this difference in pressure is less than negligible.

The second equation of Mallard and Le Chatelier differs from the first in that it makes no mention of the diameter of the tube. They sought to eliminate this

factor from the problem. Davy¹ had shown that for any mixture there is a limiting diameter beneath which this type of propagation cannot take place; and Schlösing and Demondésir⁷⁰ had found that the propagation takes place at higher and higher speeds as the diameter is increased from this limit. Mallard and Le Chatelier⁷⁰ explain these kindred facts by the observation (originally, perhaps, due to Blochmann¹¹) that flame cannot touch a cold solid; so that the shell is always surrounded by "a very thin annular zone of unburned gas-mixture in which there is a gradient from the temperature of the wall to the temperature of inflammation. The gas in this annulus escapes combustion until it has diffused into the hot gas." "Extinction is the more easily achieved the nearer the mixture to the limit of inflammability and the greater the ratio of the cold annulus to the cross-section of the tube. This ratio increases as the diameter of the tube lessens and as the flame-speed lessens." They conclude

that T will not be affected when $\frac{k}{rv}$ is negligible as compared with the specific heat of the hot gases: that is, when r and v are sufficiently large. Now r is the radius of the tube, v the speed of the flame and k is "a certain coefficient of conductivity" which is thus eliminated with benefit by the use of a tube that is suitably wide.

Thus the material of the wall of the tube has no influence or an influence within experimental error. A further interesting "conclusion to be drawn from this work is that the diameter necessary for the complete absence of drag-by-cooling is the bigger the smaller the flame-speed; and that the diameter causing immediate extinction is the smaller the bigger the flame-speed". As to the ratio between the two diameters for any given mixture, the one for no propagation, the other for completely free propagation, it differs little from 5: "in other words, if we take a tube of diameter five times the limiting diameter, we can be pretty sure of

finding ourselves working under the same conditions as if we employed a tube of a diameter indefinitely large".

This freedom, however, does not result in making the recorded speed independent of the diameter of the tube. Mason and Wheeler⁷¹ show that there is a progressive parallel increase up to the highest diameter taken, which

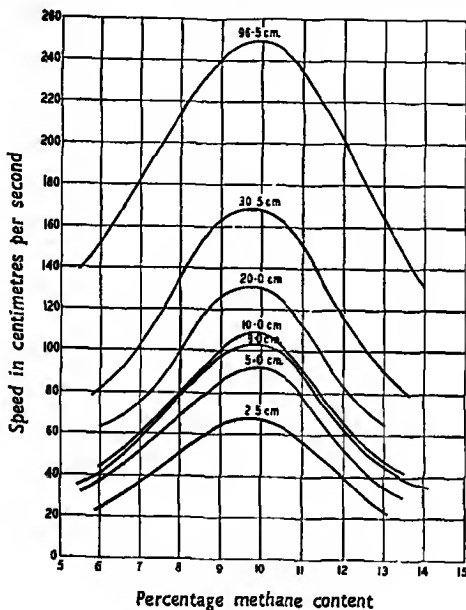


FIG. 2

was 96.5 cm. (see fig. 2). Using a 10% methane-air mixture, Chapman and Wheeler⁷³ found their results nearly expressed by the equation $V = c.D^k$, where c and k are constants. It has been shown by Coward and Hartwell⁷⁴ that the results would probably be the same in all tubes wider than 20 cm. in the absence of some factor which becomes increasingly prominent in tubes

of more than 15 cm. diameter. "The nature of this factor was first indicated by an obvious contrast between the photographs of the uniform movement in narrow and in wide tubes." The one is smooth, the other crenellated. For the same mixture, the one does not cant as much as the other. Both differences are due to convection, to the lift of the hot gases. Both differ-

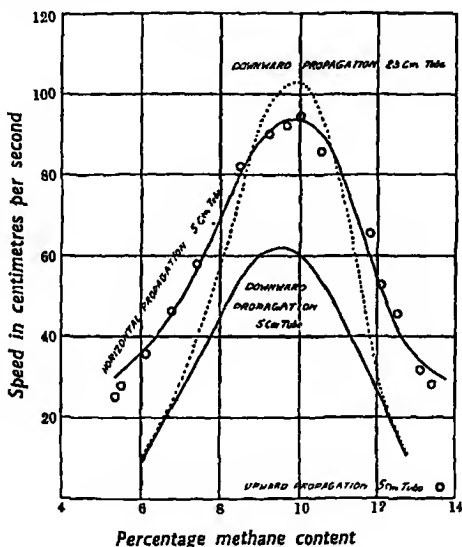


FIG. 3

ences involve a greater proportional area of the flame-shell in the wider tubes.

The great importance of convection had already been demonstrated in Mason and Wheeler's extensive investigation of the effect of differences in the orientation of the tube (see for example fig. 3). As to the length of the tube, Mallard and Le Chatelier observe that the distance travelled by the flame during the uniform

movement increases not only with the diameter but with the length ⁷⁰, "up to a point, after which no useful purpose is served by increased length. The useful length increases as the diameter increases."

Numerous published results (see fig. 4) relate to tubes of 2.5 cm. diameter and 150 cm. in length, but the

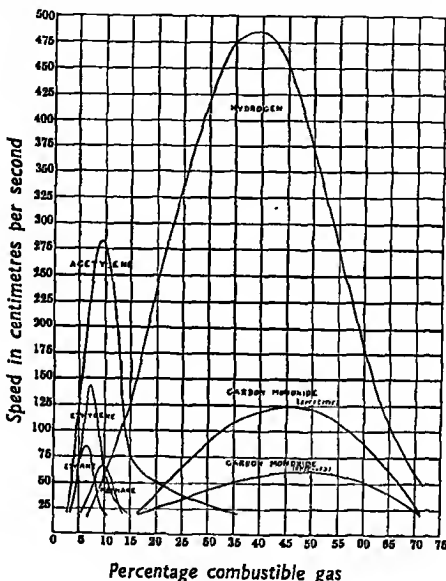


FIG. 4

generalisations deduced are independent of these particular experimental conditions. For example, such tubes were employed to test the generalisation of Payman and Wheeler as to the speed of flame in mixtures involving blends of fuels, but exceptions to the application of the generalisation do not refer to the type of flame movement. It is true, for example, of all blends of saturated paraffins. It has been stated thus ⁷⁵:

Given two or more mixtures of air or oxygen with different individual gases in each of which the speed of propagation of flame is the same, all combinations of the mixtures of the same type (all containing excess of oxygen, or all containing excess of combustible gas) propagate flame at the same speeds under the same conditions of experiment.

Ignition Within a Tube

Many results relate also to the shell that is carried out of the tube (or towards the far end of a closed tube) under the expansive force of its products, to which is added the speed of its propagation into the unburned gas, i.e., the speed that is governed by the surface-area of the shell and the fundamental speed of the mixture. A large portion of the unburned gas then leaves the tube ahead of the flame and is mixed with the atmosphere. The student is warned against the pitfall of supposing that the gas ahead of the flame-shell is in a state of rest. There is a gentle gas-flow, demonstrated by Coward and Hartwell⁶¹, even under the conditions of "the uniform movement". Consider now the conditions where the tube is closed at the firing end and the flame-shell has moved half-way along the tube towards the other end which is open. If there is no movement in the unburned gas, then the column of burned gas, in a tube open to the atmosphere, has been raised to a temperature of some 1500° C. without expansion. This of course is absurd. Actually we can demonstrate the expulsion of the unburned gas by stretching a soap-film across the open end of the tube, and a shadow-photograph measures the extent of the growth of the bubble that takes place before the flame reaches it³. When the tube is open to the air a Schlieren snapshot is a very simple means of demonstrating the expulsion of unburned gas ahead of the flame⁵⁷.

A similar movement in the unburned gas takes place when the far end of the tube is closed. The pressure rises throughout the tube, but the rise in the unburned gas is brought about by a shift of gas; the rate of this shift at any point being measured by the earliest move-

ments of "marker-flames" started independently at selected point-times in the unburned gas. It is proportional to the distance of the point considered from the original flame-shell³.

Three general truths from Chapter I will explain much that is common to the selected examples that follow³.

1. The flame, as a source of pressure, tends to move to a position where the resistance to its pressure will be everywhere equal.
2. Any cooling contact provides an area of adhesion, since over this area energy is lost, while everywhere else at the surface of the burned gases energy is being liberated.
3. The gas outside the flame-shell is moving outwards under the expansion brought about near the surface. The gas inside the flame-shell is moving inward under the expansion brought about near the surface.

Ignition in a Tube open at both ends

If in all other respects also the ventage is equally free at both ends, the flame-gases expand to atmospheric pressure equally in both directions. If the tube is long in comparison with the diameter, there is a momentary check on the expansion; since the barrel of the flame-surface makes contact with the wall of the tube. Instead of the elongation by expansion of an unbroken single surface of flame enclosing the flame-products, we have thenceforward two septums of flame-surface each of which propagates towards its own end of the tube with a velocity equal to the velocity due to the net expansion of the cooling interior gases plus the velocity that is governed by the surface-area of the septum and the fundamental speed of the mixture.

Central Ignition in a Tube closed at both ends

The burned gases within the flame expand towards whatever is the pressure to which their expansion has already compressed the unburned gases outside the

flame. The pressure-gradient is thus much less steep than in the last example, and the recorded movement of the flame-shell gradually diminishes (in comparison with its rate in the last example) until it is markedly less; the rate of this diminution depending upon the length of the tube. The axial diameter to which the flame expands before the check also depends upon the length of the tube; it can never be greater than when the tube is open at both ends. After the check, each septum of flame-shell is usually a flanged cone, the apex pointing inward, this increase in area assisting to make good the sudden discrepancy that occurs between the pressure within the flame and the pressure without when the long barrel of luminous surface, which has till now completely enveloped the burned gases, itself burns out against the wall of the tube.

Asymmetric (axial) Ignition in a Tube closed at both ends

The mass-centre of the flame moves centrewards until the check occurs. Thereafter the two residual septums of luminous surface burn towards the appropriate ends at such speeds as would seem destined to complete the two tasks at the same instant. The septum having the longest distance to travel is usually a flanged cone, but the other is often ellipsoidal. The difference is due to the difference in the amounts of unburned gas involved in the inward backflow that is necessary to equilibrate the pressure-loss in the cooling burned gases between the two septums of luminous surface.

Interior (axial) Ignition in a Tube open at one end

The mass-centre of the flame moves towards the atmosphere with the gas-flow until the check occurs. When the check occurs, the burned-out barrel of the flame is held by the area of adhesion, but the residual luminous surface facing the atmosphere is still assisted by the outward flow until it passes out of the tube;

the residual luminous surface facing the closed end burns against the gas-flow as in the Uniform Movement.

End (axial) Ignition in a Tube open at one end

This is a condition not covered by the last example. The flame is never a sphere, nor is the luminous surface at any time a continuous surface enveloping the burned gases. It is a dome which elongates rapidly as its circular base increases towards the cross-section area of the tube. The barrel then collapses, and this is the first of many checks. Mallard and Le Chatelier called this *Le Mouvement Saccadé*.

End (axial) Ignition in a Closed Tube

This differs from the last example in proportion to the length of the tube. The growth of the dome is also dependent on the length of the tube; since the pressure developed at the flame-surface is shared between the burned and the unburned gases in proportion to their volumes. (Certain minor corrections involving cooling surface and flame-shape are here ignored.) When the barrel of the dome collapses, the residual surface moves for some time at a constant speed towards the far end of the tube, its shape being usually that of a flanged cone.

It will be clear that, other things being equal, the initial speeds in these various examples must necessarily increase with decrease of diameter or with increase of length. The slowest axial speed would be given by a tube approximating to the compactness of a sphere, that is, a square cylinder. The check or arrest, which ushers in the second phase, is due fundamentally to the disposal of the pressure generated at the flame-surface. When the volume of the flame is half the volume of the container, the greater share is thenceforth exerted inward, not outward. The greater share may be exerted inwards earlier, however, if owing to the narrowness of the vessel, there is an earlier cooling contact which exacts—for the continuous equilibration of pressure throughout the tube

PROPAGATION FROM CENTRE OF SPHERE ~~41~~

—an increased direction of the generated pressure inward.

It will be clear that any comparisons of the speed at which luminous surface moves along the axis in different mixtures must be based on experiments carried out under conditions that have rigidly been kept the same. Comparisons have usually been limited to a selected distance of the run of the flame in one direction during the first phase, that is during the period that elapses before the check. Even so, the diameter, length, orientation, sparking position and sparking energy must remain identical in all experiments; and, if end-ignition is employed, the material of the tube must also be the same, since owing to the rising pressure the cooling by contact at the wall of the tube is no longer negligible.

Propagation from the Centre of a Sphere

The third method of registering speed that we have mentioned is to record the movement of flame from the centre of a sphere towards the wall. This method is applicable only to mixtures in which the propagation is developed at the same speed along every radius. If the record is symmetrical when the moving drum has a vertical axis, the method is suitable; since this is full evidence that the buoyancy of the flame due to gravitation may be neglected. The temperature and pressure rise throughout, and they are at a maximum at the moment when the luminous spherical flame-surface expires at the spherical wall. If the sphere has radius R , and the radius of the flame at time t is r , then if u is the mean rate of the movement of the flame through the medium over time t ,

$$r = ut + k. \int_0^r \left(\frac{R-r}{r} \right)^3$$

The term u differs from v , the fundamental speed, in that the layer being ignited at any moment is greater

in area than the igniting layer; it differs also in correspondence with the changing temperature and pressure.

The second term of the expression expresses the fact that the pressure developed at the flame-surface at any moment is shared between the burned and the unburned gases in proportion to their volumes. When the volume of the flame is half the volume of the container ($r = 0.794R$) there is no abrupt check or arrest, but the rate of change of recorded speed is at a maximum, and we have in the odograph a "point of inflection" ⁷⁶.

The recorded speed of the flame becomes approximately equal to the rate at which the hot gases can expand to atmospheric pressure in the ideal circumstances where the hollow sphere is not rigid but can be indefinitely expanded without work. These circumstances are closely approached in the contrivance of Stevens ⁷⁷, where a sparking-plug is introduced through the blower, which it closes, into the interior of a soap-bubble containing the explosive mixture.

The Movement of Flame through Still Gas

The Detonation Wave is the sole example of this. Having been set up, it travels at a speed some eight times as fast as the progress of the outer edge of any disturbance that may already have been created in the explosive mixture. Once it has overtaken and passed this outer edge, it moves through mixture that is at rest.

It supervenes upon the other type of propagation that we have studied, when the pressure attained in the flame-surface reaches a critical value that is characteristic of the mixture ²². This pressure, as we have seen, is exerted both upon the burned gas and upon the unburned gas that lies between the flame-surface and the outer edge of the acoustic disturbance. The compression at any point in this unburned gas varies as its distance from the flame-surface and is highest in the gas adjacent to the flame. This gas is heated both by contact and by the compression, so that its ignition is

hastened; the communication of pressure is thus accelerated and layer after layer of gas then "spontaneously" ignites under the adiabatic compression. There is a back-kick through the burned gas, and this is the Detonation Wave⁷⁸. This is the simplest example of what may become a highly complex problem, and much investigation is still in progress. The discovery of Campbell, Woodhead and Finch, that the detonation-wave may follow a helical path⁷⁹ along the tube containing the mixture has for the time being put back into the melting-pot the numerous formulae that have been advanced to express its speed.

There are certain fundamental ideas, however, that must find their recognition in any final settlement. Berthelot⁴⁵, the discoverer of the phenomenon, said that it appeared to be due to the transmission of the successive shocks by the molecules of the gas and that it was comparable to the speed of sound or to the speed of translation of the gaseous molecules as determined from their absolute temperature. He later inclined to the latter explanation. The speed would then be given by the equation of Clausius⁸⁰, in metres per second, as

$29.354 \sqrt{\frac{T}{\rho}}$, and the molecules considered would be those newly formed in the reaction. This formula approximates closely to the experimental results for many mixtures. The speed of sound itself was preferred by Mallard and Le Chatelier and by Dixon. This gives results some 30% lower than the previous method; they are very close to the experimental results for many other mixtures. Dixon's formula is

$$0.7 \times 29.354 \sqrt{2 \left\{ \frac{Q}{MC_p} + t_0^0 \text{ abs.} \right\} \left\{ \frac{\text{final vol.}}{\text{initial vol.}} \right\}^{\gamma-1}}$$

the mean density of unburned and burned gas

where MC_p refers to the products, and the volume ratio refers to measurement under similar conditions.

Payman⁸¹ has investigated the inception of the

detonation-wave in gaseous mixtures and has developed a method for photographing the invisible shock-waves or compression-waves that pass through the gas during the pre-detonation period. In fig. 5 is shown a diagram, traced from an actual odophotograph, of the setting-up of detonation in the mixture $C_2H_4 + 3O_2$, ignited 5 mm.

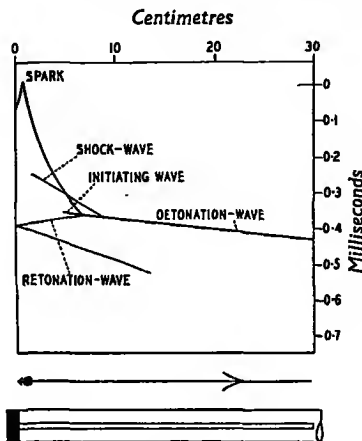


FIG. 5

from the closed end of an iron tube a metre long and 2.5 cm. wide. The compression-waves—which have such a marked effect in increasing the speed of the flame and, ultimately, in initiating the detonation-wave—appear to originate in the gases through which the flame-surface has passed and to travel at speeds much greater than is the speed of sound in these gases.

The Vibratory Movement

Certain explosive mixtures do not detonate under any known condition. Other mixtures appear easily to pass into this phase as the flame moves away from the closed end of a tube. When flame moves inward from the

open end of a tube, the necessary critical pressure in its surface is brought about during a phase intermediate between The Uniform Movement and Detonation. When the speed of the flame in its uniform movement is high, the pressure-conditions in the tube can no longer continuously adapt themselves to the increasing penetration of the flame ; and the flame-surface itself suffers vibrations of small amplitude. Their frequency is given by the period equation of C. H. Lees ⁸²,

$$\frac{\cot n \xi}{C_1} = \frac{C_2}{C_1} \tan \frac{n(L - \xi)}{C_2}$$

where ξ = distance of the flame-shell from the open end,

C_1 = mean speed of sound in the burned gas,

C_2 = mean speed of sound in the unburned gas,

$\frac{n}{2\pi}$ = the fundamental frequency of the vibrations,

L = the length of the tube.

This is an equation which Coward and Hartwell ⁷⁴ find in good agreement with their results for tubes of 10 to 20 cm. diameter and 5 to 10 metres in length. When the vibrations become finite the flame-shell is affected, suffering distortion, increase in area and therefore also increase in the rate of generation of the pressure. Conditions must thus mount to a climax. Meanwhile, the following relations have been advanced ²⁸ for shorter tubes of diameter of the order of 5 cm. :

$$\frac{n\xi}{C_1} = \pi$$

$$n = \frac{\pi(C_2 + 2 C_1)}{2L}$$

$$\frac{A - A_0}{n} = \text{const. where } A \text{ is the amplitude}$$

of the vibration and A_0 is a constant. The climax may be an expansion that causes a percussive expulsion of burned gas from the tube, or it may be the inception of the Detonation Wave.

CHAPTER III

THIS chapter is concerned largely with the processes through which an explosive mixture of gas may pass before it becomes flame. Much of it refers to experiments where the explosive mixture is contained at low pressures in vessels which are gradually raised in temperature. The results of such work are often so suggestive that they may be discriminately and tentatively applied to other conditions of ignition and to the more leisurely examples of the actual "propagation" of flame. For the sake of clearness, much of the treatment is quite elementary.

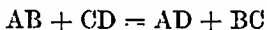
Mechanism of Gaseous Explosive Reactions

From the point of view of the electronic theory of atomic structure and valency, chemical combination can be of two kinds, polar and non-polar. The purely electrostatic attraction between ions that are oppositely charged constitutes the "polar linkage" of Berzelius. Non-polar linkage is the sharing of a pair of electrons by two atoms. In the gaseous state, the majority of reactions involve the rearrangement of non-polar linkages; and atoms which have become chemically combined by the sharing of an electron are to be regarded as being held together very firmly. On the Bohr theory of atomic structure, the extra-nuclear electrons describe orbits round the nucleus; and the sharing of an electron by two atoms can be regarded as meaning that the two atomic nuclei are encircled by its orbit. A later view of atomic structure is based on the application of wave mechanics by Schrödinger. From this standpoint the

electron is regarded no longer as a point charge but as a 'cloud' of electricity, to which the classical equations of wave motion can be applied. The possible quantum states appear as various solutions of an equation, and Schrödinger's "electric density" at any point corresponds to the probability that the electron in any given atom is at that point. In this way the mutual action of two atoms can be calculated by combining their wave equations. If, for example, we consider two neutral hydrogen atoms, it is found that they may react upon one another in two ways: one of the solutions of the equation gives repulsion at all distances; but the other fixes a certain distance between the two atoms at which the mutual potential energy is at a minimum. At this point there is a position of equilibrium and the two atoms can combine to form a molecule.

Energy of Activation

In a bimolecular reaction of the type



it is only possible for the new molecules AD and BC to be formed if it is at least just as easy for A to combine with D, and B with C, as it is for the original molecules to be re-formed. This rearrangement of the atoms in the molecules AB and CD can be regarded as possible if, by means of sufficiently strong vibrations of the molecules at the moment of collision, the atoms A and B, and C and D have become separated to a certain definite extent. The minimum potential energy involved in this exchange may be regarded as the energy of activation of the reaction. Hence chemical reactions such as $2CO + O_2 = 2CO_2$ in which there is a rearrangement of non-polar linkages, require the prior communication of a certain amount of energy to the molecules that are to take part in the reaction.

Starting from general thermodynamical considerations, van't Hoff⁸³ established the well-known law for

the temperature dependence of K , the equilibrium constant, namely,

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

where Q is the heat of reaction. In 1889 Arrhenius⁸⁴ found that the influence of temperature on reaction velocity can be expressed with great accuracy by the equation

$$\frac{d \log k}{dT} = \frac{E}{RT^2}$$

where k is the velocity constant of the reaction, and E is a definite constant for every reaction and has the dimensions of energy. If R is taken as 1.98 calories, then E is measured in calories per gram molecule. According to Arrhenius, this equation represents the shift in the equilibrium between the two kinds of molecules that are present in a chemical reaction, namely the normal and the 'active' molecules. It is the 'active' molecules alone which take part in chemical reactions; and E ("energy of activation") in the Arrhenius equation may be identified with the energy that is absorbed when a normal molecule becomes an activated one. It follows also from Le Chatelier and Braun's "principle of mobile equilibrium" that an increase in temperature will favour the formation of 'active' molecules and so increase the rate of reaction.

In homogeneous gas-reactions that are purely thermal, such as combustion in the flame-surface, activation may be brought about (1) by collision, and (2) by absorption of radiation. It seems probable that activation results chiefly from the inelastic collision of two molecules that, relatively to each other, have a sufficiently high energy of translational motion, this being converted into energy of activation.

Considering $A + B \rightarrow AB$, the possibilities of reaction are—

- (1) Molecule A alone is activated: $A^* + B$.
- (2) Both molecules A and B are activated, but separately: $A^* + B^*$.

- (3) A + B are activated simultaneously by collision together.

According to Hinshelwood⁸⁵, it is the last possibility which is most likely to occur.

Types of Molecular Energy

We have used the terms "translational energy" and "internal energy of activation". The first—often written k —is the energy that the molecule possesses in virtue of the translational motion of its whole mass, and it is manifest in temperature and in pressure (energy of impact at the wall). There are three types of internal energy: the vibrational energy (v) refers to the vibration of the nuclei within the molecule, and is connected with the absorption and emission of radiation in the infra-red; the rotational energy (r) is an additional energy possessed by virtue of the rotation of the nuclei as a pair about their centre of mass, and changes in this give rise to bands in the far infra-red; the electronic energy (e) is the energy of the extra-nuclear electrons, and the results of change are radiations in the visible and ultra-violet regions of the spectrum.

Rôle of Vibrational Energy in Activation

In the process of chemical activation it is the vibrational quanta which are important. From a study of spectroscopic data it appears that at the frequency corresponding to the convergence-point of the vibrational bands, the energy that is absorbed as radiation represents the minimum amount required to bring about dissociation of the molecule: but before this level is reached, sufficient vibrational energy may be imparted to a molecule to loosen the atoms and to bring about in the molecule the necessary condition for chemical reaction.

Rôle of Translational Energy in Activation

The energy of activation appears to originate in the translational energy *along the direction of impact*; that

is, only in the translational component along the line joining the centres of gravity of the colliding molecules. The portion of the kinetic energy which is involved is expressed in terms of the *square* of the component of the molecular velocity in this direction. Thus for two molecules in collision, the total energy for the purpose of activation involves two "square terms", or two "degrees of freedom". The number of molecules possessing sufficient energy to become activated is $Ze^{-E/RT}$, where Z , the "collision number" (i.e. the number of molecules colliding in 1 c.c. per second), is $\sqrt{2}\pi\sigma^2\bar{u}n^2$, where σ is the effective diameter, \bar{u} is the root mean square velocity, and n the number of molecules in 1 c.c. If all the collisions between molecules which have been sufficiently activated result in chemical reaction, then the velocity of reaction is equal to the number of molecules involved in such collisions; that

$$\text{is,} \quad \frac{dx}{dt} = Ze^{-E/RT}$$

Whatever may be the origin of the energy of activation its mechanism consists in a redistribution of the excess energy of the system, resulting in an increase of the vibrational energy of the colliding molecules. Simultaneous with this, the chemical rearrangement occurs, involving electronic displacements; and new molecules are formed, possessing an amount of kinetic and internal energy in excess of the normal. This excess internal energy is often dissipated in the form of radiation.

Chain Reactions

It has been found that a large number of chemical reactions have velocities which are much greater than can be accounted for on the theory of reaction by kinetically activated molecules. Now the velocity equation of Arrhenius applies to an initial chemical reaction, but only rarely in the combustion of gases is this the principal reaction. In general, the energy evolved by the initial reaction brings about a reaction velocity far in excess of the initial velocity. This may

be due to the conversion of chemical into kinetic energy ; on the other hand, there may be completely new reactions initiated as were the "chain" reactions postulated by Bodenstein ⁸⁶ in the photo-chemical formation of hydrochloric acid.

Researches on the kinetics of various gas-reactions that occur in a heterogeneous phase at comparatively low temperatures have shown that with increasing temperature the same reaction progressively exhibits a tendency to the evolution of a homogeneous phase. The effect of the walls of the reaction-vessel as the focus of reaction-centres gradually diminishes during the transition ; and on occasion they are even capable of exercising a reverse, anti-catalytic, effect. For these walls, which at relatively low temperatures behave exclusively as catalysts, may, as the temperature increases, deactivate to a greater and greater extent the larger number of reaction-centres obtained in the homogeneous phase. As the temperature gradually approaches the ignition-temperature of the gas-mixture, the whole mechanism of reaction becomes more and more complex, and this is exhibited by marked increases in the reaction velocities ; such increases cannot be explained on the basis of the Arrhenius equation by the dependence of reaction-velocity on temperature. They are, however, satisfactorily explained by a theory of chain reactions, due to Christiansen and Kramers ⁸⁷, and later applied to explosive reactions by Semenov and his co-workers.

Semenov ⁸⁸ has shown that in many instances both slow (i.e. flameless) combustion and explosion can be explained by reaction-centres and branched chains. If the reaction-centres are removed by the walls of the experimental vessel as fast as they are formed there will be a uniform rate of reaction ; on the other hand, if the heat produced is sufficient to form a large number of reaction-centres, or if the chains branch to a large extent, explosion will occur.

The distinctive feature of a chain reaction is that the primary activation of a comparatively small number of

molecules results in a communication of some of the acquired internal energy to a much larger number of other molecules, leading to reaction velocities that are much greater than those calculated from the Arrhenius equation.

In chain reactions, the rate of reaction varies with time even if the concentration of the initial substances is kept constant and the products of reaction are removed. Two very important features of chain reactions are the marked effects of the slightest traces of some specific substances, and of the walls of the experimental vessel, upon the rate of reaction.

Every chain reaction exhibits some of the following criteria—

- (1) In photochemical reactions there is a considerable quantum yield.
- (2) In thermal reactions, a decrease in dimensions of the vessel retards the change by lessening the distance the reaction-chains can traverse before reaching the wall. Thus, in tubes, chains starting in the gas and broken at the walls should show a rate of reaction proportional to the square of the radius of the tube.
- (3) Conversely, the addition of an inert gas may accelerate the reaction. Oxygen often has a small influence and may even retard oxidation.
- (4) The rate of reaction is abnormally influenced by the concentrations of the reacting substances. This is because the concentration affects not only the number of chains starting in unit time, but also the successfulness of their propagation.
- (5) Traces of certain foreign substances show a marked inhibiting or accelerating effect on chain reactions.
- (6) In chain reactions a period of induction may often exist; and further progress of the reaction takes place according to curves of the type $1 - e^{Qt}$ or e^{Qt} , where the reaction-rate is an explicit function of the time.

One of the most remarkable phenomena of chain reactions is that of the critical pressure-limits of ignition. On passing these, a very slow reaction suddenly changes into explosion. The critical limits may be upper limits or lower limits. Fig. 6 shows the three pressure-limits of ignition that exist within the indicated range of temperature for a mixture of methane and oxygen in proportions for complete combustion. These have been investigated by Neumann and Serbinoff⁸⁹. The lower ignition-limit is represented by the curve AB (above

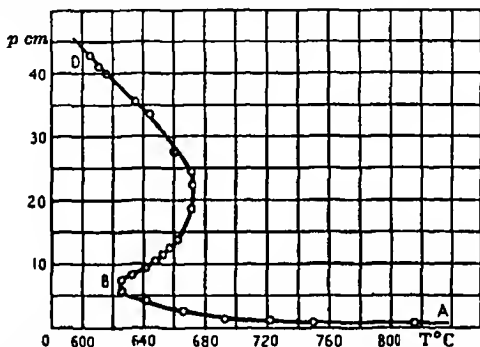


FIG. 6.—Region of inflammation of the mixture $\text{CH}_4 + 2\text{O}_2$.
(Neumann and Serbinoff)

which an ignition occurs), the upper limit by the curve BC, and a third limit by CD. A non-stationary explosive process is only possible to the right of the curve ABCD; to the left of it, there is only a reaction that is negligibly slow.

Chains may start either in the gas or at the walls of the vessel. They may be stopped:

- (i) by collision in the gas, with the elimination of an active molecule owing to the formation of a new chemical substance,
- (ii) by collision in the gas, with "physical" de-activation of an active molecule,

(iii) by collision of an active molecule with the walls of the vessel,

(iv) by chemical reaction on the walls of the vessel, involving the removal of an active molecule.

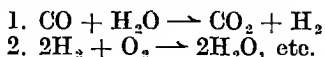
Chains may be classified as 'energy' chains or 'material' chains. In an 'energy' chain the links are excited molecules of a reactant or product, and in 'material' chains it is some definite new molecule or radicle which is responsible for carrying on the reaction. A material chain will be broken and deactivation will occur by the elimination of a molecule or radicle.

Effect of Moisture on Combustion

An early material-chain theory is contained in the dictum of Mrs. Fulhaue ¹⁵⁹, that "water is decomposed in every instance of combustion". This may be an overstatement, but it foreshadows a discovery of fundamental importance made by Dixon a century later ⁹⁰. Bunsen ⁹¹ had noticed that steam oxidised red-hot charcoal to CO. Grove found that at a high temperature steam oxidised CO to CO₂. Buff and Hoffmann showed that the high temperature was unnecessary if a mixture of the reagents were continuously sparked. In 1875 Grove's discovery was independently repeated by Horstmann ⁹² and also by Dixon who in 1880 found that a mixture of carbon monoxide and oxygen that had been in contact with phosphorus pentoxide for a considerable time would not explode when an ordinary secondary spark from an induction coil was passed through the mixture. The addition of a trace of moisture or of any gas that contained hydrogen at once rendered the mixture explosive.

Dixon investigated the influence of the moisture-content of a mixture, $2\text{CO} + \text{O}_2$, on its mean rate of flame-propagation and found that the velocity of flame was lowered as the drying was increased. He showed that while the ignition-pressure of electrolytic gas was unaffected by damp, CO exploded with defect of O₂ in a wet eudiometer, yielded more CO₂ than twice the

oxygen used. This catalytic effect on the speed of flame was explained by Dixon as being due to the action of steam in the following way :



For some time it was considered that carbon monoxide and oxygen were incapable of direct combination, and that moisture was necessary for the combustion of such a mixture. In 1886, however, Dixon observed that "in the explosion of cyanogen with an excess of oxygen, the formation of carbonic acid is complete, and is not affected by the presence of moisture". Ten years later, Dixon, Strange and Graham found that the flame in the explosion of a well-dried mixture of cyanogen with twice its own volume of oxygen, "does not appear to differ from the flame given by the same gases mixed with 1.5 per cent. of water", and they conclude that "in a mixture of freshly-formed carbon monoxide and oxygen, these gases unite as the mass cools down without the intervention of steam; and where steam is present it does not appreciably alter the time during which the change continues" (see also p. 81).

Weston⁹³ has made an investigation of the flame spectra of carbon monoxide and of hydrogen, and also of mixtures of the two in varying proportions. From the results he obtained, together with the fact that mixtures of carbon monoxide and oxygen that had been dried for two years over phosphoric oxide could still, with a sufficiently powerful igniting spark, give rise to flame, Bone⁹³ concludes that in a flame of undried carbon monoxide two sets of independent reactions occur simultaneously, namely: (1) a dry reaction, in which direct interaction occurs between carbon monoxide and oxygen, giving rise to the continuous and banded parts of the spectrum, and (2) a reaction catalysed by steam, in which CO and H₂O molecules interact and give rise to the 'steam lines' in the spectrum.

Garner⁹⁴ and his co-workers found that in explosions

of mixtures of carbon monoxide and oxygen there was an intimate relationship between the speed of flame and the emission of radiation. They showed also that with 1.9 per cent. water vapour present in a $2\text{CO} + \text{O}_2$ mixture the fraction of the energy that was emitted as radiation was only about one-quarter as much as for gases that had been dried for 2 hours over phosphoric oxide; moreover, the speed of flame was over 1000 cm. per sec. in the moist gases, as compared with a value of about 100 cm. per sec. under the same experimental

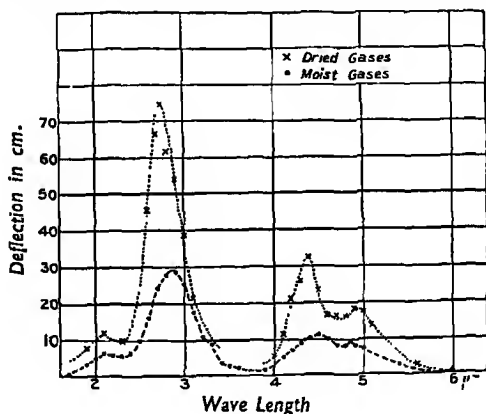
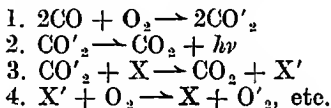


FIG. 7

conditions in the dried gases. Hydrogen, and hydrogen-containing substances, were found to act similarly to water not only in promoting an increased speed of flame but also in reducing the amount of radiation emitted. The explosion-flame in mixtures of carbon monoxide with oxygen emits the major part of its infra-red radiation in two bands, with maxima at $2.8\ \mu$ and $4.4\ \mu$. These are both emission and absorption bands of carbon dioxide. The diminution in emission at these two maxima when water-vapour is present in the mixture is shown in fig. 7. This represents the spectrum

in the infra-red region for moist and dried mixtures $2\text{CO} + \text{O}_2$ as obtained by Garner and Johnson. Garner and Roffey suggest that these effects of hydrogen or water-vapour may be due to physical processes, rather than to the catalytic process of a chemical nature suggested by Dixon. The hydrogen, or the water-vapour, may in some way retain within the system energy which otherwise would be emitted as radiation; and a typical mechanism, involving collisions of the second kind, is shown in the following four serial equations:



This chain mechanism indicates how the freshly formed (1) molecules of carbon dioxide which have become activated by the chemical reaction, may be deactivated by emission of radiation (2), or by collision with molecules of a third substance (3) which then transfer their energy to one of the reactants (4).

Ignition

The lowest temperature at which chemical reaction in a given gaseous medium becomes self-sustained is usually termed the "ignition temperature". It is not a well-defined physical constant, since it is dependent, amongst other things, on the way in which the heat is conveyed to the gases. This temperature does not necessarily correspond with the actual appearance of flame, since on many occasions there is a "pre-flame period" during which the reaction is self-sustained. Smithells⁶ has defined the true temperature of ignition as that "at which the reaction proceeds at a rate just sufficient to overbalance the loss of heat . . . from the burning layer of gas, so that the next layer is put in the same state, and steady combustion proceeds".

All modes of ignition can be regarded as supplies of

heat to an explosive mixture for a definite period of time. Ignition may be brought about by :

- (i) direct contact with hot reactive gas, as in an ordinary flame,
- (ii) direct contact with hot inert gas,
- (iii) direct contact with an incandescent surface, e.g. a wire,
- (iv) gradual heating of the mixture in a vessel,
- (v) adiabatic compression, the ignition being due to heat produced by mechanical work,
- (vi) an electric spark of sufficient energy, viz. :
 - (a) impulsive electric discharge,
 - (b) break spark, or momentary arc,
 - (c) spark on fusion of heated filament.
- (vii) mechanical or chemical actions which produce gas at high temperatures, e.g. smouldering ; match-striking ; the action of moisture on pyrophoroi, alkaline metals and organo-metallic compounds ; the action of chloric acid on sugar.

In considering the process of ignition by various methods it is necessary to distinguish between those in which combustion is homogeneous, being uninfluenced by the presence of any surface, and those in which combustion is heterogeneous. In the latter case, the attainment of ignition-temperature is more rapid, in consequence of the "catalytic" action of a solid surface, than it would be if the gas were at the same temperature but not in contact with the surface. In such heterogeneous reactions the nature of the surface, whether smooth or rough, is of great importance in its effect on the speed of reaction.

As examples of the first type of ignition, a lamp flame or the flame projected from a solid explosive or from an auxiliary explosion vessel^{17, 95} may become a source of ignition provided that it is sustained for a sufficiently long time. Walls and Wheeler⁹⁶ and Rintoul and White⁹⁶ have studied the ignition of firedamp by momentary flames. It is found that the requisite duration of exposure of the inflammable mixture became less as the flame used became larger (see also pp. 82-4).

Effects of Solid Surface

Ignition temperatures and the lag on ignition have also been determined when the combustion has been surface-catalysed. Taffanel and Le Floch ⁹⁷ and Wheeler with Mason ⁹⁸ and with Naylor ⁹⁹ have used quartz vessels for such investigations. (See fig. 8, later.)

A further example of this type of ignition is the initiation of combustion in inflammable mixtures by wires carrying an electric current. They provide—as Thornton ¹⁰⁰ showed—not only a source of heat, but also a surface-catalysis.

Ignition of the inflammable mixture in which the wire is placed may occur without any fusion of the wire, or it may occur only when fusion takes place. In either case surface-combustion will have altered the composition of the gas-mixture in the immediate neighbourhood of the wire before ignition occurs. The amount of surface-combustion will depend to a great extent on how long the current has passed before ignition takes place. For this reason, amongst others, “fusion sparks” do not cause ignition as readily as “break sparks”.

For ignition by wires of a material that undergoes rapid oxidation, the period of oxidation must be greater than the ‘time-lag’ of the particular mixture. Further, with filaments that undergo oxidation extremely slowly, ignition does not precede fusion, unless the temperature of the wire is higher than the ignition-temperature of the mixture. The results show that the period of possible contact between wire and gas is diminished to a very small value, unless the wire is placed vertically, because of the induced convection.

Shepherd and Wheeler ¹⁰¹ have carried out investigations on the ignition of methane-air mixtures by heated platinum and tungsten wires, and they conclude that there are two main determinant factors. First, the amount of heat in the wire and its temperature depend upon the value of the electric current, and on the nature and dimensions of the wire. Secondly, ignition may be

effected by the additional heat which is developed through the catalytic combustion of the inflammable mixture on the wire itself. In the case of ignition of mixtures of methane and air by tungsten wires, the wire is oxidised until a bright flame results, and this is often the actual cause of the ignition.

Adiabatic Compression

The ignition-temperatures of mixtures of gases have been determined chiefly by one of two methods, the adiabatic compression method, or the concentric tube method. The former was suggested by Nernst, and experimented with by Falk¹⁰², and later by Dixon¹⁰³ and by Tizard¹⁰³; the ignition-temperature is calculated from the observed minimum compression required to ignite the mixed gases, using the formula

$$\frac{T_2}{T_1} = \left[\frac{V_1}{V_2} \right]^{\gamma-1}$$

where T_1 and T_2 are the initial and final temperatures (on the absolute scale), V_1 and V_2 the initial and final volumes of the gaseous mixtures, and γ is the ratio of the specific heat at constant pressure to that at constant volume. The position of γ in the volume-term makes the method very much dependent on an accurate evaluation of specific heats.

Concentric Tube Method

The method employing two concentric tubes is more direct for obtaining ignition-temperatures, and is the method used at the present time for such determinations. In principle, it resembles the Argand burner. It was devised for Dixon¹⁰⁴ in 1903 by Foster and developed by Coward; it consists essentially in the separate pre-heating of the combustible gases before they are allowed to mix at the temperature of the enclosure. The influence of heated surfaces in promoting pre-flame combustion is thus to a large extent eliminated. The temperature of each stream is slowly raised until flame

appears in the zone where they meet, the temperature of ignition being recorded by a platinum resistance thermometer placed near the outlets whence the two streams issue. In the latest form of the apparatus for Dixon's later work with Higgins, and for the more recent investigations of Coward, the outer silica tube into which the air or oxygen is passed has been made much wider, so that an appreciable interval occurs before the mingling gases come in contact with the solid wall. The inflammable gas is passed in through a central quartz tube. The flame is observed through a glass window at the top of the furnace. The clay furnace-cylinder is enclosed in a steel outer case which permits the pressure to be varied.

The Lag on Ignition

Dixon's papers direct attention to the dependence of ignition-temperatures on the lag ; for, as Mallard and Le

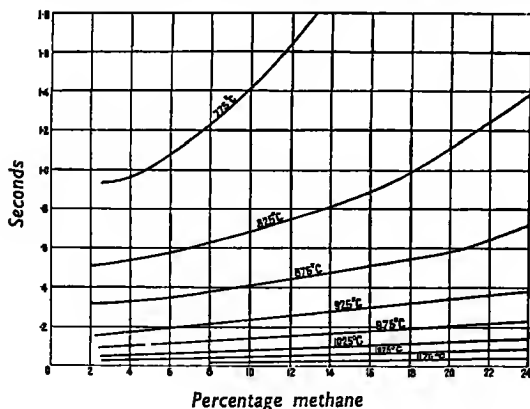


FIG. 8

Chatelier had shown, after an explosive mixture has been heated to its minimum ignition-point, there may be an appreciable interval of time before flame appears.

Consequently in determinations of ignition-temperatures this lag is timed. Some results of Naylor and Wheeler⁹⁹ in the investigation mentioned on p. 59 are shown in fig. 8. The lag represents a period of pre-flame combustion, and its duration is dependent to a great degree upon the particular conditions of experiment.

The following experimental results of Dixon show the relationship between 'lag' and the observed ignition-temperatures :

TABLE I¹⁵⁸
EFFECT OF 'LAG' ON IGNITION-TEMPERATURE

Gas	Lag sec.	In Air ° C.	In Oxygen ° C.
Hydrogen . . .	{ 0.5	630°	625°
	{ 5.0	588°	588°
	{ 10.0	577°	575°
Methane . . .	{ 0.6	746°	666°
	{ 2.0	710°	641°
	{ 10.0	657°	602°

The relation between the ignition-temperature and pressure for various periods of lag when the explosive mixture was one of hydrogen with air is shown in fig. 9, prepared by Coward¹⁰⁵ from Dixon's results.

One result of the existence of the lag on ignition is that a source of heat at a temperature much higher than the ignition-temperature may be briefly introduced into a gas-mixture without causing ignition. It is primarily due to the very short time of contact, that frictional sparks can be showered into certain inflammable mixtures of gas without igniting them so long as the sparks are moving rapidly through the mixture. Sometimes also, while the temperature of a spark is high enough to cause ignition, its heat capacity is not sufficient to maintain this temperature long enough.

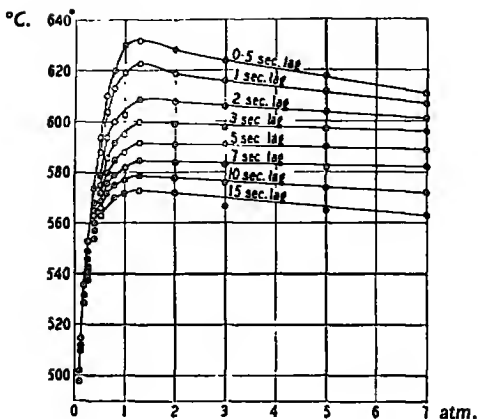


FIG. 9

Mechanism of Ignition

Up to about 1910 it had been assumed generally that both ignition and propagation were purely thermal. In that year Sir J. J. Thomson¹⁰⁶ suggested that high-velocity electrons "may precede the explosion wave, and prepare the way for it by ionising the gas". Work on the ionisation of gases had given some slight evidence that ionised molecules were specially reactive in chemical change. Moreover, since it was becoming recognised that chemical combination is essentially connected with the transits of electrons in the reactant molecules, it became natural to look for some definite connection between ionisation and the processes of chemical activation in determining the ignition and inflammation of combustible gas-mixtures.

Many investigators (Thornton¹⁵, Wheeler^{16, 110}, Morgan¹⁰⁷, Finch¹⁰⁹ and others) have worked on the ignition of explosive mixtures by electric discharges; and from their researches it has become evident that the amount of heat required to ignite a given mixture varies with the character of the igniting agent. When a pure

condenser-discharge is used, the amount of heat required is less than when the spark employed is produced by the separation of contacts in an inductive circuit. This again is less than when a hot wire is the igniting agent. Such experimentally determined facts have led some workers to consider that ignition by an electric discharge cannot wholly be explained by a thermal theory. Yet these facts are not inconsistent with the idea that an important factor in ignition is the rate of input of energy, that is, the rate of heating: the more slowly heat is applied to a combustible gas-mixture the greater is the amount required to bring about ignition; this is because heat is dissipated by conduction, convection, and radiation to the surrounding parts of the experimental vessel, and to the remoter parts of the gas-mixture.

It is the view of Taylor-Jones, Morgan and Wheeler¹⁰⁸ that ignition depends upon heating a sufficient volume of gas to a sufficient temperature. It was found, in comparing the effects of induction-coil sparks with those produced by discharge of a condenser, that the most effective spark for ignition is that which heats the greatest volume of gas to the ignition-temperature. Thus the results of these experiments favoured the thermal theory of the ignition process.

Morgan¹⁰⁷ has also carried out experiments with gas-mixtures which lie outside the dilution-limits of inflammability, and has found that the amount of combustion with a constant spark gap was proportional to the heat-energy of the spark; conversely, that with a constant spark-discharge, it was proportional to the width of spark gap. Moreover, he was unable to detect any ionisation when using a platinum wire heated (but not glowing) by an electric current to bring about combustion in a weakly inflammable mixture of coal-gas and air. Morgan considers that these experimental results definitely point to heat as being the sole cause of combustion.

Taylor-Jones¹⁰⁸ has set down the view of those who hold the thermal theory of ignition. "The thermal theory states that if a certain minimum volume,

characteristic of each explosive mixture, is raised to the ignition temperature, the flame so formed will spread throughout the gas. The importance of thermal conduction in the theory is that it enables the 'minimum volume' to be raised to the required temperature more easily with some sources of heat than with others, but it is not suggested that thermal conduction, or the translational energy, plays any particular part in the chemical reactions which occur when that temperature is reached."

Considerable work has been done by Finch¹⁰⁹ and his co-workers on the 'cathodic' combustion of hydrogen and carbon monoxide in a direct-current discharge at reduced gas-pressures. As a result of their early experiments in which they took the view that thermal effects were eliminated, they concluded that ionisation was the determining factor in combustion, since the rate of combustion under these conditions was proportional to the current. After further work, especially dealing with the combustion of carbon monoxide, they concluded that these reactions occurred homogeneously; and that combustion was dependent upon a suitable prior excitation of the reacting molecules, a sufficient concentration of suitably activated molecules determining the ignition. Work under similar conditions by Guénault and Wheeler¹¹⁰ showed that a temperature-rise of several hundred degrees could be produced by the discharge, and suggests that its ability to cause chemical reaction by electronic excitation of the molecules may be assisted by its thermal effect. As a result of later work on oscillatory discharges, Finch found that the discharge-frequency exerts a greater effect on the igniting power of sparks than the potential energy that is contained in the condenser prior to discharge; the greater the frequency of the discharge the higher is the level of activation. Morgan has pointed out, however, that actually Finch and Thompson's experiments show that the igniting agent was more powerful when the frequency was lowered. Further, Morgan suggests that these results of Finch and Thompson are quite in keeping with a

thermal theory of ignition ; the increased incendivity obtained with the lower frequency is due to the increase in the energy that is dissipated in the form of heat in the initial part of the spark, the total heat energy of the spark being without significance.

The juxtaposition of so-called thermal and electrical theories to explain the mechanism of ignition by an electric discharge is somewhat misleading. Chemical reaction is the essential precursor to ignition ; and before this can take place some molecules of the combustible gases must have their internal energy increased, or be activated. This can be brought about in other ways than by simply increasing their translatory energy, as some have imagined the thermal theory implies, and it is very probable that, *initially*, the molecular kinetic energy in the electric discharge can be disregarded as being at all an important factor in activation. The conditions of an electric discharge constitute in themselves, at least at first, the molecular conditions, i.e. the raising of electronic levels with ultimate ionisation, that are requisite for chemical reaction. This process of "electrical" activation will apply only to a very small number of molecules. The heat developed by the reaction between these first few molecules will then result in such an increase of kinetic energy that activation will take place through collision and lead to chemical reaction. There will be, however small, a lag on ignition by electric discharge as in any other method of ignition, and the apparent effect of this lag will be, as the thermal theory postulates, that a certain minimum volume of combustible gas-mixture must be heated to a sufficient temperature. The ignition of gas under these conditions, in the mass, appears explicable on the thermal theory, assuming activation to take place through collision ; but the source of heat that brings about general ignition is initially developed by reactions between molecules that have previously been activated "electrically". The results of experiments with a flow system by Lewis and Krentz ¹⁶⁰ indicate that if one of

the constituents is subjected to a spark-discharge, the ignition-temperatures of methane mixtures are lowered during a short immediately subsequent period.

As to the general preparation of the gas for combustion, information is beginning to accrue from application of the method of absorption spectroscopy.

Egerton and Pidgeon ¹¹¹ have examined the absorption spectra of hydrocarbons (propane, butane, pentane, etc.) in mixtures in which combustion was just beginning. Ultra-violet light was passed through quartz windows in a long experimental tube which was maintained at various temperatures between 230° C. and 490° C. Absorption bands were found in the far ultra-violet, being identified as those of formaldehyde. Absorption in this region was proved to be due mainly to the formation of acids. For many years investigators have reported the presence of HCHO in the condensates of incomplete combustion.

Withrow and Rassweiler ¹¹² have studied the absorption spectra of gases in an internal combustion engine. Evidence was obtained of chemical reaction in the non-inflamed gases which were the last to be burned and prior to the occurrence of "knocking". In particular, there was absorption in the region of the spectrum between 2800 and 3600 Å, a banded structure being superposed on the continuous absorption in this region, and indicating the formation of formaldehyde. Owing to the temperature of the absorbing HCHO being raised, the bands were wider in the engine spectra than in the usual formaldehyde spectrum.

Limits of Inflammability

When speeds of flame of mixtures of a combustible gas with air or oxygen under given conditions are plotted against the percentage fuel-content of the mixture, a curve is obtained showing a maximum and also two limits, where the limbs of the curve end abruptly at concentrations of the inflammable gas which are termed the lower and upper limits of inflammability

under the given conditions. Through mixtures within these limits, but not through mixtures outside them, self-propagation of flame will take place after ignition has once been effected. A limit-mixture can be defined as one in which the heat developed by the combustion of each layer of mixture is just sufficient to ignite the adjacent layer. Most results, however, refer to experimental conditions in which the flame-surface does not, throughout, enclose the gas already burned; hence for any particular gas the limits of inflammability vary slightly with the position of ignition. The progress of the septum of flame-surface is assisted or retarded by convection or, more strictly, by gravitation, according as it is made to spread into unburned mixture that is respectively above it or below it. The widest range of inflammability therefore occurs with upward propagation of flame, and the narrowest with downward propagation; with horizontal propagation the values are intermediate. For the same reason, the limits vary slightly with the size and material of the vessel in which the experiments are conducted, and moreover, because of the influence of the prevalent pressure, are dependent upon whether the vessel is open or closed. Turbulence of the gas-mixture has a marked effect on the values for the limits of inflammability, increasing the liability to ignition from a strong source and diminishing the liability to ignition by a weak source.

Coward and Hartwell¹¹³ have shown that when diluents are added to mixtures of methane and air the extinctive powers shown by such gases are chiefly (i) the reduction in oxygen-content of the mixture by the added diluent, (ii) its thermal capacity, and (iii) its thermal conductivity.

The effect of increasing the initial temperature is, as might be expected, to widen the limits of inflammability. An increase in initial pressure narrows the range of explosibility of mixtures of air with most gases at the lower limit, but may narrow or extend the range at the higher limit depending upon the particular combustible gas^{114, 115}.

TABLE II

RANGES OF EXPLOSION IN AIR: PERCENTAGE COMPOSITION
FOR DOWNWARD PROPAGATION

Gas	Temperature: Atmospheric Pressure : Atmospheric	Temperature: 100° C. Pressure : Atmospheric	Temperature: Atmospheric Pressure : 10 atmos.
Hydrogen . . .	9.0 to 68.5	8.8 to 73.5	9.5 to 67.5
Carbon monoxide . . .	15.9 to 72.9	14.8 to 73.7	18.4 to 62.4
Methane . . .	6.0 to 13.0	5.95 to 13.7	6.6 to 14.0

By rapid compression to a figure of the order of 300 atmospheres, Harwood and Dixon¹⁰⁴ have produced visible flame in all mixtures of methane and air between 2% CH₄ and 75% CH₄.

Many investigations have been concerned with series of mixtures in which the inflammable gas was burned not merely with air nor with oxygen, but with "atmospheres" of arbitrary oxygen-content which was varied, and with "atmospheres" in which nitrogen was replaced by other diluent gases. One graphical method of exhibiting the results of such work is due to Leprince Ringuet¹¹⁶, who conveyed his information on the limits of inflammability in mixtures of methane, oxygen and nitrogen by plotting the ratio CH₄ : O₂ against the ratio N₂ : O₂. A further complication is introduced if more than one inflammable gas is present in the series of mixtures. Le Chatelier's¹¹⁷ general rule for calculating the limits of inflammability of complex gases may shortly be stated thus: if n' n'' n''' are the percentages of different combustible gases in a limit-mixture, and N' , N'' , N''' . . . the limiting percentages taken separately, then

$$\frac{n'}{N'} + \frac{n''}{N''} + \frac{n'''}{N'''} + \dots = 1$$

Jorissen¹¹⁸ has devised a graphical method of repre-

senting the limits of inflammability of two gases or vapours, either or both combustible, with oxygen or with air. The co-ordinates represent the concentrations of the gases. If the mixtures obey Le Chatelier's rule, the upper and lower limits of inflammability are indicated by straight lines. When the experimental results do not agree with the formula, the lines are curved. An example of Jorissen's method is shown in fig. 10 which refers to mixtures of hydrogen and ammonia with

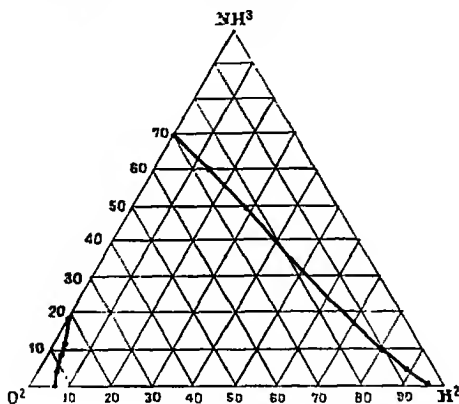


FIG. 10

oxygen; the space between the two lines is the "region of explosion".

Le Chatelier's rule holds generally for both upper and lower limits. White^{115, 119} finds the following exceptions: hydrogen-ethylene-air, hydrogen-sulphide-methane-air, hydrogen-sulphide-hydrogen-air, and all mixtures that contain either CS_2 or any other constituent that can propagate a phosphorescent flame (see p. 71). Coward and Jones¹²⁰ find that dichloroethylene-methane-air constitutes a further exception.

It is this rule, applied to faster mixtures, that becomes the Speed Generalisation of p. 37.

Determinations of the limits of inflammability in tubes are made in tubes sufficiently long to allow of observers judging if the mixture were capable of continued self-propagation of the septum of flame-surface. The range is naturally extended to some degree by extending the diameter of the tube. The "caps" and "flares" in "ultra-limit mixtures", mixtures outside the range, are mentioned on page 2. The "cap" of flame from a spark is quite soon extinguished after floating up from the source of ignition.

Phosphorescent Flames

It has long been known that the slow oxidation of phosphorus is accompanied by a greenish luminescence, which in air under reduced pressure begins at $7^{\circ}\text{C}.$, very much below the temperature at which it catches fire, $60^{\circ}\text{C}.$ This is probably the earliest recognised example of chemiluminescence. Chemiluminescence is radiation that directly results from chemical change. In most bimolecular processes, chemical reaction only occurs between suitably activated molecules that result from the unordered heat motion of the molecular system. In this way an ordinary thermal reaction is brought about. When the new molecules that are produced as a result of the reaction are activated, the energy of activation may be converted into radiant energy. In this chemiluminescence, the activated product of the chemical reaction may itself be the emitting unit, or it may, by collision, transfer an excess of energy to another molecule. In such a case, the latter is the emitter; and chemiluminescence that is produced in this manner may be called "sensitised".

Davy¹²¹ observed that ether vapour in the neighbourhood of a hot platinum wire was phosphorescent, and since that time many so-called "cold" flames have been obtained. Their temperature is so low¹²² that thermal emission is negligible; yet they have shown a decided luminescence. Frankland¹²³ in 1862 found that the

vapour of carbon disulphide in air becomes phosphorescent when brought into contact with a heated surface at 149°C . and that a trace of ethylene destroyed the luminosity. In 1890 ¹²⁴ Turpin found that the slow combustion of carbon disulphide began to be perceptible at 100° , producing a red-brown solid together with sulphur dioxide. The red-brown solid has since been shown to be CS ; and Dixon ¹²⁵ found that the phosphorescence and the formation of CS were interdependent. Dixon attempted to explain the inhibitory action of ethylene and other substances by assuming that these poisons condense on the CS molecules first formed and prevent their attacking CS_2 molecules, so that the larger particles, which seem necessary for the production of the phosphorescent flame, are never formed.

Several of these chemiluminescent reactions in cool flames have been studied by Emeléus ¹²⁶. Phosphorus trioxide and phosphine, under suitable conditions, were found to give phosphorescence at 30° – 40°C . and 160° – 230°C ., respectively. The ultra-violet band spectra of these substances burning in oxygen or air are both identical in their main features with that of the oxidation of phosphorus. Moreover, Emeléus has found that this band spectrum is obtained both in the cool flame when phosphorus burns in air under reduced pressure (125°C .) and in the much hotter flame at 800°C . From these results it would appear that the molecular species emitting the light is the same in all cases. Of sulphur also, and of arsenic, it is true that the chemical reactions are not dependent on whether the flame is normal or phosphorescent. It is now generally thought that the chemiluminescent oxidations of phosphorus, arsenic and sulphur are energy chain reactions, the velocity of which depends essentially on the transference of energy liberated in a primary process to neighbouring reactant molecules, which are thereby activated. The spectra of the cool flames of carbon disulphide and ether, however, are different from the spectra of their normal flames, especially so in the case of ether. Emeléus, on

examining the phosphorescent combustion of acetaldehyde, propaldehyde and hexane, found that the same band spectrum was given by each, but that it did not correspond with any known carbon system. He came to the conclusion that acetaldehyde probably played no essential part in the luminous oxidation of hexane and propaldehyde. It is, however, still uncertain to what the light emission in these flames is due. It is possible that the radiating molecules are connected with the "active" molecules and "peroxides" which have been postulated in connection with these reactions; on the other hand, the phosphorescence may be quite a secondary effect.

Highly Diluted Flames

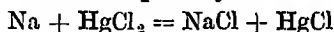
When the vapour of alkali metals is allowed to react with the halogens, and with mercuric halides, at low pressures of the order of 10^{-3} mm., a cool, highly diluted flame is produced. Since 1928 Polanyi^{127, 128} and his co-workers have carried out several investigations on these atomic reactions, and have adduced important conclusions about the velocity of the chemical reactions that are involved. Since the mean free path of the molecules is several centimetres they study a flame of considerable length. A deposit of alkali halide forms on the wall of the tube in which the reaction takes place, and the distribution of this deposit yields the requisite data for calculating the velocity of the gas stream, the intensity of the emission, the partial pressures of the reacting substances, the reaction velocity and details of the mechanism of reaction. In many of these reactions, chemical change results at *every* collision; that is, they are reactions between atoms and molecules in which the energy of activation of the process is zero. The flame produced is of a true chemiluminescent nature, since on account of the good thermal conductivity at the low pressures that are employed, the flame temperature, usually about 300° , is below that at which radiation in the visible spectrum is perceptible.

Two types of reaction yielding these highly diluted flames may occur. Examples of the first type are :

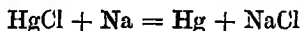


Taking sodium and chlorine as an example, it is found that the primary reaction is $\text{Na} + \text{Cl}_2 = \text{NaCl} + \text{Cl}$. It appears that every collision in such a reaction is effective. The majority of the chlorine atoms formed in the primary reaction appear to unite with sodium atoms on the wall of the tube, and no light is emitted in this process. The reaction $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$ takes place in the gas phase ; the NaCl molecules thus formed are activated, and collision with Na atoms causes an emission of the sodium D line.

The second type of reaction is exemplified by the reaction between sodium vapour and the vapour of mercuric chloride. The primary reaction is



followed by



in the gas phase.

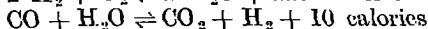
This type of reaction differs from the first type in that heating the reaction zone does not diminish the emission of light as occurs when the $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$ reaction zone is heated, owing to the dissociation of the sodium molecules.

CHAPTER IV

THIS chapter is concerned largely with the processes that take place in the gas immediately following the passage of the flame-surface.

Displacement of Maximum Pressure

The release of available energy is not immediately complete in the layer of gas-mixture which, having accepted, now relinquishes the rôle of flame-surface. For if this were true, then P_m (see Chapter I and § "Rise of Pressure", page 11) would be a measure of the calorific value of an explosive mixture. That this is not so is shown by the fact that mixtures giving greatest P_m in a fuel-air series, all centrally ignited in a sphere, contain a greater percentage of fuel than the mixture in which the fuel is molecularly balanced against the oxygen for complete combustion. Such mixtures are: 35.5% CO (Balanced mixture 29.45% CO)¹²⁹; 34.1% H₂ (Balanced mixture 29.45% H₂)¹²⁹; and 10.3% CH₄ (Balanced mixture 9.45% CH₄)⁷. This displacement of the maximum pressure only falls short of an independent rigid proof of a delay in the completion of the thermo-chemical equations in that we have at present no information as to the losses of energy by radiation during the spread of the flame. We know however from other considerations that the composition of the gas through which the flame has passed must tend to the following equilibriums¹³⁰:



Equilibrium Shift

These equilibria are not stable in the conditions of explosion. The influence of rising temperature is to push them all towards the left so that the temporary concentration of the final products is diminished. The influence of rising pressure is to push the first two of them towards the right, so that the temporary concentration of the final products is increased. If the pressure in the explosion-vessel rises from 1 atmosphere to, say, 6 atmospheres, then at some intermediate pressure, say 4 atmospheres, there is a release of energy due to the shift of equilibrium in gas that has already suffered the passage of flame at a lower pressure, say at 2 atmospheres. After P_m has been passed, the antagonism of the rising temperature is no longer operative and the thermo-chemical equation is rapidly completed.

Consider, however, a number of mixtures that burn towards an equilibrium of the same final products that is not affected by pressure-changes and is only slightly affected by changes in temperature.

Different Behaviour of Comparable Gas-mixtures

One may compose a group of mixtures all of which would yield the same maximum pressure if the results of the two following factors were negligible: loss of energy by radiation during the flame-period; delayed completion of the thermo-chemical equation. Moreover, if the results of two further factors were negligible, pressure would be developed at the same rate in all the mixtures; and the pressure-time curves would be similar in every respect. These further factors are: differences in thermal conductivity and in rate of reaction; differences in the rate of change in the number of molecules present.

With the same reservations, one may compose a second group of mixtures, all of which would yield the same maximum temperature, T_m .

If there be chosen a series of mixtures of fuels with

oxygen that will contain the same number of units of carbon, hydrogen and oxygen, their calorific values may be adjusted by dilution; and one mixture, in which there is no change in the number of molecules, may be common to both groups. Such mixtures are:

GROUP I (a) (Calc. P_m 137 lbs.)

1. $C_2H_2 + H_2 + 2 O_2 + 20.15 A$
2. $2 CO + 2 H_2 + O_2 + 2.45 A$
3. $CH_4 + CO + 1.5 O_2 + 7.26 A$
4. $C_2H_4 + 2 O_2 + 16.01 A$

GROUP II (a) (Calc. T_m 2788° Abs.)

1. $C_2H_2 + H_2 + 2 O_2 + 20.15 A$
2. $2 CO + 2 H_2 + O_2 + 5 A$
3. $CH_4 + CO + 1.5 O_2 + 6.31 A$
4. $C_2H_4 + 2 O_2 + 14.47 A$

Or if for argon there be substituted a proportion of ($CO_2 + H_2$), then—with the reservations stated—every part of the contents of the sphere would at P_m be intimately concerned in the "water-gas equilibrium". Then we have—

GROUP I (b) (Calc. P_m 137 lbs.)

1. $C_2H_2 + H_2 + 2 O_2 + 3.39 (CO_2 + H_2)$
2. $2 CO + 2 H_2 + O_2 + 0.36 (CO_2 + H_2)$
3. $CH_4 + CO + 1.5 O_2 + 1.345 (CO_2 + H_2)$
4. $C_2H_4 + 2 O_2 + 3.0 (CO_2 + H_2)$

GROUP II (b) (Calc. T_m 2788° Abs.)

1. $C_2H_2 + H_2 + 2 O_2 + 3.39 (CO_2 + H_2)$
2. $2 CO + 2 H_2 + O_2 + 0.84 (CO_2 + H_2)$
3. $CH_4 + CO + 1.5 O_2 + 1.06 (CO_2 + H_2)$
4. $C_2H_4 + 2 O_2 + 2.433 (CO_2 + H_2)$

In all, we have 8 mixtures calculated to give the same P_m as $C_2H_2 + H_2 + O_2 + 20.15 A$, and 8 mixtures calculated to give the same T_m as this mixture. They should all, *ex hypothesi*, burn to an equilibrated system

of end-products that is unaffected by change in pressure, namely, $\text{CO} + \text{H}_2\text{O} + k(\text{CO}_2 + \text{H}_2)$.

Small differences between calculated and observed values for pressure and so on would have little significance in view of our imperfect knowledge of specific heats and of the indeterminacy of the value of k , which has been taken as 4.* But if the data employed were significantly inaccurate, we should find in the results a large persistent difference between corresponding members of the a groups, diluted by argon, and the b groups, diluted by $(\text{CO}_2 + \text{H}_2)$ wherein the whole body of the diluent gas enters the equilibrium and is affected by the equilibrium constant. A difference of this order does not appear. The results are characteristic of the basic mixtures employed, rather than of the diluents.

Mixtures thus calculated were prepared dry over mercury and fired at the centre of a dry spherical container 19.77 cm. in diameter. The dissimilarity of the pressure-time curves that were obtained is gross, as is shown by Ellis's records in Table III.

* For example, if we use the equations suggested by Hahn ¹³¹ (which themselves were built up on experimental values of specific heats) from his first equation,

$$\log k = -\frac{2232}{T} - 0.08463 \log T - 0.0002203T + 2.4943$$

we find $k = 6.13$

and from the modified equation,

$$\log k = -\frac{2226}{T} - 0.0003909T + 2.4506$$

introduced by him because of the unsatisfactory character of the results obtained by the first equation for temperatures above 1100° C., we find

$$k = 3.65$$

But this equation assigns k a maximum (at 2386° Abs.) of 3.844, which does not agree with the experimental determinations of Dixon, of Smithells, or of Andrew ¹³². The existence of this maximum, moreover, is dependent on the dissociation of CO_2 and H_2O (suppressed on the hypothesis of completed combustion at maximum pressure) which is fundamental to the Hahn equation.

TABLE III
THE EXPLOSION OF GASEOUS MIXTURES ⁷

Mixture		P _m calc. (lbs.)	P _m (lbs.)	T _m calc. (° C. above lab.)	Flame- period (centi- seconds)
Group	No.				
Ib	2	137	110.5	2930	0.5
Ia	2	"	115	2880	0.636
Ib	1	"	110	2495	1.4
Ib	4	"	113.2	2240	4.07
Ia	1	"	107.5	2495	4.46
Ib	3	"	113	2309	4.87
Ia	4	"	110.7	2370	9.05
Ia	3	"	110.3	2386	15.04
IIb	2	116.5	97	2495 (2788° Abs.)	0.576
IIa	2	123.3	105	"	1.05
IIb	1	137	110	"	1.4
IIb	4	154.4	126	"	2.68
IIb	3	149.2	122.5	"	3.264
IIa	1	137	107.5	"	4.46
IIa	4	144.8	120	"	6.31
IIa	3	142.6	116	"	7.23

Differences in flame-period may be expected to relate chiefly to differences in the rate of reaction as shown in fig. 11, which gives the curves for mixtures IIa.2 and IIa.3. Ellis has taken the flame-period as unity for the purpose of comparing two curves, this meaning that for one of the curves the scales must be multiplied by factors dependent on differences in the rate of reaction; this graphical treatment then brings into prominence such facts as are shown in fig. 12, where the less simple mixture is shown to release a less proportion of its energy in the early stages, and a greater in the later stages, than the mixture that proceeds by a shorter route to complete combustion.

These curves show, therefore, that two mixtures of equal calorific value and equal heat capacity (and therefore equal temperature of combustion) reach their

maximum pressures by notably different paths. This result cannot at present be attributed solely to any one of the factors that we have named; but it would

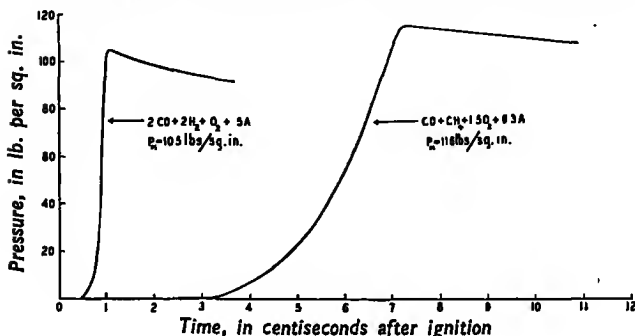


FIG. 11

evidently be explained by specific delays (characteristic of the respective mixtures) in the completion of the thermo-chemical equation.

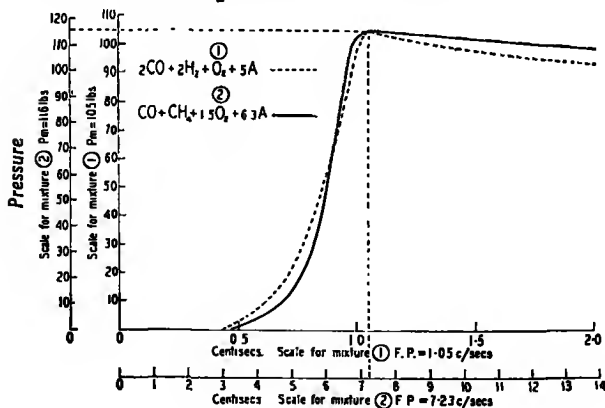


FIG. 12

Afterburning

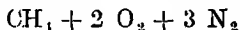
Clerk's¹⁷ description of this was "Afterburning"; and to understand his intention in using this term it must be remembered that at that time "burning" signified the process of oxidation with emission of heat and light and the ability to communicate combustion; except high temperature, no source of light was known. Thus the word "burning" involved no consideration of atoms built up on a Bohr-Rutherford model, nor of the modern explanation of quantised radiation. To Dixon also the gas through which the detonation flame had passed was "still burning"⁷⁸.

Dixon must also have intended to convey by the word a certain activated condition, for he says: "In a mixture of freshly formed CO and oxygen, these gases unite as the mass cools down without the intervention of steam; and where steam is present it does not appreciably alter the time during which the change continues. This result agrees with Professor Smithells' ⁶ observation that when a dried mixture of cyanogen and air is burnt in his 'separator', the CO formed in the inner cone will burn in dry air, provided the outer cone is kept close to the inner; but when the cones are widely separated, so as to allow time for the CO formed below to 'settle down', the outer flame is extinguished by bringing it into dry air."

It has been shown that in the gas within the flame there is indeed a delayed completion of the emission of heat and light, a reactive condition, and an ability to communicate combustion; as to the completion of the oxidation, however, there is no completely decisive evidence of any extensive lag behind the appropriate equilibrium position. There is no spectrographic evidence whatever of the presence in the burned gases from mixtures of hydrocarbons with oxygen of anything besides the hydroxyl radicle and linkages of CO and oxygen which are in process of becoming carbon dioxide.

Incendivity of the Gas within the Flame

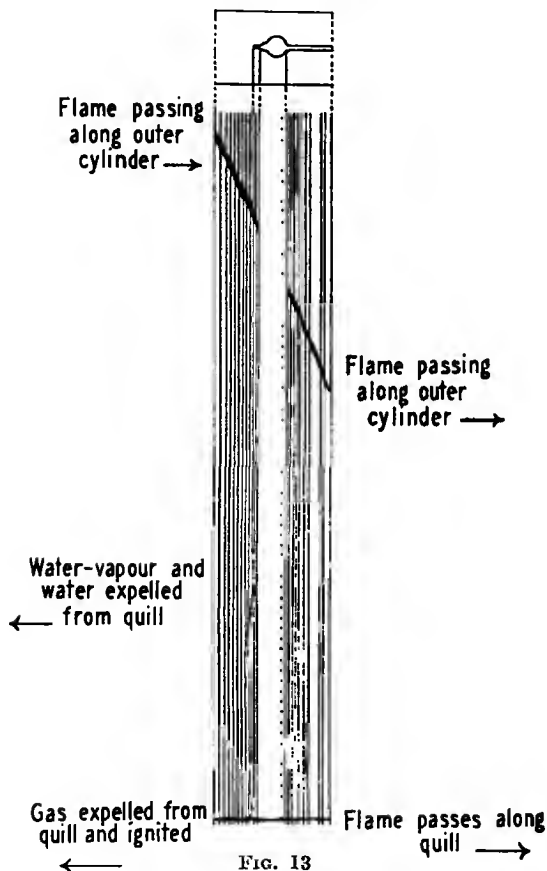
The incendivity of the flame-gases has been demonstrated⁷ by Ellis, but it cannot easily be assessed. Gas from the interior of a flame is not differentiated from inert gas by the mere fact that it will ignite fresh explosive mixture. Argon, suddenly compressed in a cylinder, one end of which accommodates a window of very thin glass, will ignite explosive mixture in an adjacent container into which it is spurted by the break-down of the window. The mixtures so ignited, however, have not included any more dilute than $2 \text{ H}_2 + \text{O}_2 + 2 \text{ A}$ and $2 \text{ H}_2 + 3.5 \text{ O}_2$. The hot argon failed to ignite $\text{CH}_4 + 2 \text{ O}_2$. The suggestion remains that there is a difference in reactivity, that is, in physical and chemical state, between the hot inert argon and the hot freshly formed (or forming) products of combustion; for the mixture



has been ignited by the end-products of a mixture of methane and air burning at atmospheric pressure; and mixtures actually of methane and air are kindled by these products if they have been produced in a closed space (where their energy has, comparatively, been conserved up to the moment of release). For if a party wall between two containers is so made as partially to break down under pressure—one way is to build into it a microscopist's cover-glass—and ignition is arranged near the wall, then after the flame has grown for some time as a dome based upon this partition the pressure—about 35 lbs. for the experiments quoted—punches out the weakest portion and is released into the adjacent container. This augmented incendivity is ascribed by Withrow and Rassweiler¹³³ to the persistence of hydroxyl radicals.

The experimental technique is simpler still when the igniting gas is fully expanded to atmospheric pressure: a flame moves inward from the open end of a tube (which may be, say, $\frac{1}{2}$ metre long and 5 cm. wide) and meets the tapered end (containing a drop of water) of

a pipette that is filled with explosive mixture (fig. 13). In a typical experiment, water and water-vapour were ejected from the pipette twenty centiseconds after the flame had reached the end of the pipette and this ejection



occupied a further twenty centiseconds. Then the contents of the pipette began to be ejected into the hot dark gas and a few milliseconds later took fire. As a lecture-experiment, the explosion may be produced quite simply by using a mixture of coal-gas and air both in the water-sealed pipette and in the open outer tube.

Delayed Emission of Heat

It has been shown by Hopkinson ³³, Mache ³⁵, David ³², Lewis ³¹, and by Ellis and Morgan ³⁴ that at any particular instant the temperature rises radially inward from the flame-surface. This result may without doubt be partially ascribed to recompression of the hot gases as soon as the pressure has risen significantly in the vessel. This does not explain however why this rise should take place quite early in the flame-period. It seems to indicate that there is a delayed emission of heat, as indeed there must be if with rising pressure there is exothermic shift in the equilibrium. Moreover Ellis and Morgan have shown that when the equilibrium-shift is endothermic this is reflected in the disappearance or reversal of the temperature gradient within the flame.

The Luminosity of the Flame-Gases. Afterglow

If a simple odophotograph be made of the ignition of $13 \text{ CO} + \text{O}_2$ at the centre of a sphere, it will be seen that luminosity is recorded as having been emitted solely from the flame-surface. Since the temperature increases inward, and since the character of any chemical reaction that proceeds in the internal gases is in this case the same as that in the flame-surface, the local pressure—which is highest at the flame-surface—would at first seem to be an essential factor in the appearance of this luminosity. On the other hand, the light-producing fall of many of the electrons towards their final orbits may be spontaneous, happening merely as the final incident in the locally intenser chemical reaction.

When the mixture is $2 \text{ CO} + \text{O}_2$, the flame is brighter

and hotter, and the pressure is higher and increases at a greater rate. Here, the gas does not cease to be luminous until the pressure and temperature have both fallen to low levels. The luminosity may be modified to some extent by firing the mixture at an initial pressure of 185 mm. The rôle of pressure as an essential precondition of luminosity in the combustion of such a mixture is suggested even more strikingly by the effect of still further reductions in the initial pressure; for a point is reached where no luminosity is photographed, either in the flame-surface or in the gas within the flame that has ceased to constitute the flame-surface, until the pressure due to the combustion has risen to an appropriate level. This level depends on the chemical character of the mixture. If, for example, the mixture is electrolytic gas, which may be suitably diluted with a monatomic inert gas, there is—as Bunsen ⁴ and as Frankland ⁵ both noticed—no appreciable luminosity until the flame-period is at an end. It must be remembered that the initial rise of pressure is comparatively slow and that, for example, the pressure rises to P_m from $P_m/2$ as the flame spreads through the last one-eighth of the diameter of the sphere. Explosions in bubbles show that without this rapid rise in pressure—and therefore of temperature—at the close of the flame-period, the sudden emission of light that often takes place generally from the entire body of the gas does not occur.

This conclusion is not limited to the condition of central ignition in a sphere; the rôle of pressure is again made clear in combustion-phenomena that are especially characteristic of tubes and cylinders. David and Davies ¹³⁴ have shown that when a mixture is fired in a cylinder and suddenly compressed by a piston after its luminosity has died away, its emission of luminosity is resumed. In a longer cylinder, repeated compressions may be brought about naturally, owing to the susceptibility of long tubes to vibration. In the odograph record of such an explosion, as in those of Woodbury,

Canby and Lewis¹³⁵, alternate light and dark bands appear, and Kirkby¹³⁶ has proved that the periodicity of this reluminescence in the gas behind the flame correlates accurately with the fluctuations in the pressure-record, as well as with fluctuations in the conductivity. Another example is provided by Kirkby's records of explosions of methane and air in a long cylinder fitted with restricting rings¹³⁶. When flame is propagated under conditions of this kind, it is shot forward as a long tongue (cf. Chapter I, § "Rise of Pressure") so that the surface of pressure-generation is greatly increased in area and the rise in pressure throughout the tube is extremely rapid. A rapid rise in pressure—and therefore of temperature—of this kind is found to cause an intense reluminescence of the gas behind the flame that has ceased to constitute the flame-surface: so intense that a cursory examination of the record might confuse it with the normal combustion of gas trapped behind the constrictions.

Local Reluminescence

With some mixtures, only a part of the gas within the flame retains or resumes luminosity. In the experience of the authors, in every example of this kind the gas involved is the gas that was burned very early in the flame-period and thus suffered its initial changes at a low initial pressure and with a comparatively low emission of light. When the explosion-vessel is a tube, the duration of this early part of the flame period, "Phase I", is more sharply bounded by the phenomenon that it has become usual to call "the flame arrest", though there is no fundamental difference from an explosion of the same mixture in a sphere. The gas involved, treated as a whole, ceases at this point to expand and is henceforth compressed towards its initial cold volume, its position being easily identified on the record by the superior luminosity that it exhibits often long before the end of the flame-period. Burned gas in the rest of the tube, or sphere, that has suffered the

passage of flame after Phase I has ended, remains dark until, just before the expiration of the flame-surfaces, there is the final rapid rise of pressure—and of temperature—to the maximum figures. Even then, especially when a tube is employed, the central gas is still separately distinguishable by its superior luminosity. Yet, in so far as it is at a different pressure from the gas compressing it, it is clearly at a *lower* pressure. Its temperature, at least near the axis of the tube, must on the other hand be higher. Evidently pressure-variation will not fully account for variation in luminosity without some reference to the chemical and physical state of the gas upon which the pressure is exerted.

The same localised luminescence may be found in the still simpler conditions characterising explosions from central ignition in a sphere. The gas within the flame may be luminous in every part until the moment of maximum pressure, when there is a general cessation of luminosity except at the centre. An example of such a mixture is $9.5 \text{ CO} + \text{O}_2$. Another type of record is obtained when the mixture consists of $2 \text{ CO} + \text{O}_2$ with a proportion of CO , O_2 , N_2 , A or He . The afterglow is seen to set in well before the flame arrives at the wall of the sphere.

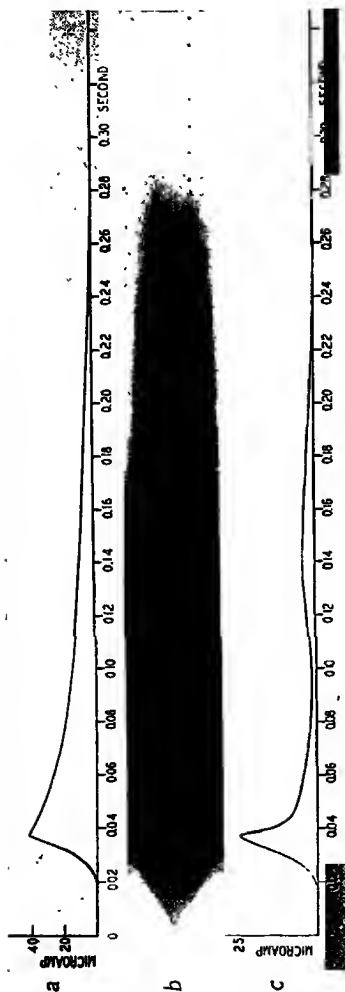
In explosions within a sphere, the second phase does not start with the same abruptness as when a cylinder is employed; Kirkby has shown that the afterglow begins gradually in a zone about midway between the centre and the sphere-wall and that it spreads immediately across the centre. Its appearance may be delayed by increasing the dilution of the reacting mixture, and the same treatment diminishes its diameter. It is usually associated with a mixture where the thermochemical equation must suffer an exothermic shift with rising pressure. It is delayed until approximately the moment of maximum pressure with mixtures of which this is not true, mixtures, for example, that consist of $2 \text{ CO} + 2 \text{ H}_2 + \text{O}_2$ diluted with inert gas. If successive

additions of hydrogen are made to a mixture of the type $2\text{CO} + \text{O}_2^{\text{dil}}$, thus changing the character of the mixture towards the type which burns to an equilibrium having an endothermic shift, the onset of the afterglow is successively delayed according to the proportion of hydrogen added. The diameter of the afterglow that appears at approximately the moment of maximum pressure may be the whole diameter of the sphere, or it may again be indefinitely reduced, or suppressed, by suitable dilution of the original mixture.

Source of the Afterglow

What is general to every example of the appearance of the afterglow in closed vessels is that it always appears to be dependent for its existence upon a sufficiently steep pressure gradient, and unless it appears at or before the moment of maximum pressure it is never produced. Under no circumstances has an afterglow been observed to start at a measurable interval after the moment of maximum pressure.

We have now to consider in what specific way the incidence of changes of temperature and pressure lead to the emission of actinic radiation from the intermediate and final products of the thermo-chemical process. The bulk of the radiation from the flame-surface is in the invisible infra-red, so that the ordinary odophotograph forms no direct register of the intra-molecular disturbances that take place in the chemical interchange. Actinic radiation emitted during the explosion has, as Garner¹³⁷ has pointed out, two possible sources. First, it must be emitted when an electron moves nearer to the nucleus of the radicle or molecule to which it belongs; and the wave-length of this radiation is characteristic of the radicle or molecule, so that by spectrography we can begin to identify the emitters responsible for the luminosity of the explosions. The second possible source of actinic radiation during the explosion—and of this no direct evidence has been found—is that which may be emitted when an electron and a positive ion



(a) Photoelectric Cell Current-Time Record of Visible Radiation.

(b) Odophotograph.

(c) Ionisation Current-Time Record.

FIG. 14.

coalesce ; emitted, that is, as they combine to form the excited neutral particle whose further emission provides a record in the spectrum. It has long been recognised that ions and electrons are present in the gas considered. It is their formation that causes the explosion-flame in an electrical field to behave, as Guénault and Wheeler¹³⁸ have demonstrated, as a light body electrically charged. Their presence is probably the result of the action of high temperature upon molecules and radicles which, having been produced in the chemical reactions, possess an excess of internal energy above their normal. Rise in pressure will increase their rate of recombination. The afterglow closely corresponds in some respects with the combination of ions, as registered in the electrical conductivity of the gas ; it is not, however, thus simply to be accounted for.

From visual inspection of the odophotographic records of explosions in a sphere, it appears that the afterglow is always most intense at the moment of the arrival of the flame-surface at the wall, that is, when the temperature and pressure attain their maximum values. In order to obtain quantitative measurements of the varying intensity of the luminosity during explosions, and for the purpose of exact correlation with the degree of conductivity, Kirkby¹³⁹ has employed a photo-electric cell. The maximum photocell current, which indicates the emission of maximum intensity of visible radiation, corresponds to the most intense region of the afterglow as photographically recorded (fig. 14). Moreover, the maximum photocell current occurs very slightly after the time of maximum conductivity, and corresponds with the steepest portion of the conductivity decay curve, immediately after its maximum. The maximum conductivity occurs at the moment of maximum temperature when the flame is just arriving at the wall of the sphere, and the concentration of ions is probably greatest at the centre of the sphere, which, from the photographic records, is the seat of the most intense luminescence. It is here that the maximum pressure,

generated in the flame-surface when the latter is just arriving at the sphere wall, becomes operative immediately after the moment of maximum temperature. At the moment of maximum pressure the ions formed during the explosion sustain the quickest rate of recombination, with consequent production of the maximum intensity of visible radiation that can be due to this source.

Abnormal Molecules

It is clear, however, that the "afterglow" can only be ascribed in small measure, if at all, to the recombination of ions. Such ions may have been produced in the formation of the molecular products as an immediate result of the chemical reaction, but their existence is due also, perhaps to a greater extent, to the effect of the subsequent rise in temperature on the products of reaction. It may be that "afterburning", when it occurs in the gases behind the flame-front, is an additional source of ionisation and hence of conductivity. Yet if a number of molecules are ionised, a much larger number must have been excited to a point falling short of actual ionisation; and the visible radiation may also be accounted for, and in greater measure, by the movement of electrons towards normal orbits in this larger number of excited molecules that are formed as a result of the reaction. It is impossible at present to assess the exact shares of the two factors, the recombination of ions and the molecular quiescence, in the production of the afterglow; but whilst there is this cognate production of ionisation and afterglow, and the possibility that the incendivity of the gases within the flame is at least increased by the presence of ions, the evidence of the formation and recombination of ions is more particularly of value in its indication of a much more widespread state of excitation in the newly formed molecules. To this, therefore, we ascribe the greater share of responsibility for the emission of the afterglow.

This conclusion is confirmed by two further investi-

gations : the first of these is spectrographic and identifies the excited molecules and radicals that are actually the sources of the luminous radiation ; the second shows that the law governing the fading of the afterglow differs in an essential manner from that governing the decay of the conductivity. The facts indicate that the afterglow is mainly due to the quiescence of electrons within their molecules towards their normal orbits rather than to the recombination of ions ; it differs from the light of the flame-surface in that the emission from the flame-surface is more largely due to the movement of electrons within radicals of transient existence that are not found in the spectrum of the gas within the flame.

Spectrography of Flame

The spectrum of the afterglow, therefore, must not be confused with the spectrum of the flame-surface. With regard to the afterglow, the spectra for methane and other hydrocarbons have much in common with those for carbon monoxide and hydrogen and the results for these two simpler gases will first be set down.

CARBON MONOXIDE. The spectrum of the afterglow of a mixture of carbon monoxide and oxygen is almost identical with that of the flame. Its features are as follows :

1. *The continuous spectrum from 2500 Å to 5500 Å :* this was first observed by Frankland ^{5, 140}, both with carbon monoxide and with hydrogen, especially under pressure. Liveing and Dewar ¹⁴¹ say that " there is not the slightest indication that this continuous spectrum is produced by the widening of the lines or obliteration of the inequalities of discontinuous spectra of the same gas at lower pressures ". This continuum tends, according to Weston ⁹³, to disappear as hydrogen is gradually added to the experimental mixture, until with the water-gas mixture it is absent. Finkelburg ¹⁴² adduces two types of change which produce continuous spectra. (a) In a reaction that involves the combination or separation of atoms, or ionisation and recom-

bination of ions, any energy in excess of that required for the reaction, or excess energy produced by the reaction, may be emitted or absorbed as a continuous spectrum. (b) In intra-atomic or intra-molecular processes in which the initial or end level, or both, are not definitely quantised, continuous spectra should be produced. In a molecule where the rotational energy alone is unquantised, each single band becomes a continuum, and a train of bands appears as a continuous spectrum. Further, if the nuclear vibrational states are unquantised, the bands become a continuous spectrum. Bone and Lamont¹⁴³ thus attribute the continuous spectrum of the carbon monoxide flame to the emission of unquantised radiation.

2. *A banded structure in the same region.* This is attributed by Kondratéev¹⁴⁴ and by Mlle. Kaczýnska¹⁴⁵ to linkages of CO and O₂ which are in process of becoming CO₂. It has nothing in common with the spectra of oxides of carbon in vacuum-tubes, an observation confirmed by Fowler and Gaydon¹⁴⁶. Apart from slight differences in relative intensities, the bands of the flame-surface are identical with those of the afterglow, at least from 3500 Å to 4850 Å. They seem to be produced by the direct combination of excited neutral molecules of CO with neutral molecules of oxygen without dissociation into atoms of carbon and oxygen or molecules of carbon.

3. *Hydroxyl bands* when the explosive mixture is moist, or when it contains hydrogen.

HYDROGEN. 1. *The continuous spectrum above 3500 Å.* This tends to be denser as the initial pressure is raised.

2. *A banded structure*, which, as shown by Bonhöffer and Haber¹⁴⁷, is due to the hydroxyl radical. This is strengthened by increasing the initial pressure.

HYDROCARBONS GENERALLY. Withrow and Rassweiler¹⁴⁸ have shown that the spectra of the flame-surface combine those of hydrogen and carbon monoxide with lines due to CH and CC. These lines do not

appear in the spectrum of the afterglow nor in the spectrum of the outer cone when the hydrocarbon is burned at a jet. The spectrum of the afterglow is emitted by the same molecules as those which give off light during the explosion of a moist or hydrogenated mixture of carbon monoxide and oxygen; and these are clearly, therefore, the principal source of the continued release of heat-energy from the gas within the flame. Vaidya¹⁴⁹ used a large Smithells Separator, and also a batwing flame, "end-on", for recording the flame spectrum of ethylene. The inner cone gave, in addition to the CC, CH and OH bands, a system of fainter bands extending from 4100 to 2500 Å. They are thought to be due to CHO.

METHANE. The observations on hydrocarbons apply to methane, the flame-surface spectrum of which has been examined by Lauer¹⁵⁰ who finds CH at 3900 Å and 4300 Å, CC at 4737 Å, 5165 Å and 5635 Å and OH at 2811 Å, 3064 Å, 3428 Å and 3471 Å. He has also established the CH band at 3143 Å, and a further hydrocarbon band CH_x at 3627 Å.

Thus the spectrum of the flame-surface shows bands characteristic of CC, CH and OH, together with the underlying continuous spectrum due to the burning of carbon monoxide. The spectrum of the afterglow shows the hydroxyl bands and the underlying continuum, but the bands due to CH and CC are absent. These results—which cannot be fitted into any simple scheme of combustion by successive hydroxylations—have been repeated by Guénault¹⁵⁷ who has added the important discovery that in the flame of mixtures of methyl alcohol having the same temperature as similarly constituted mixtures of methane, the CC bands are very much less intense.

From Kirkby's¹⁵¹ results on the fading of the afterglow it is evident that the decay of ionisation is not directly related to the decay of radiation in the visible region. Fig. 15 shows two synchronous records of an explosion in a glass sphere of a mixture $2\text{ CO} + \text{O}_2$

that had been dried over phosphoric oxide. A is the curve of the radiation in the visible region of the spectrum and was obtained by the use of a photoelectric cell. B is the curve of the ionisation current. There is a pronounced lack of similarity in character in the two curves in the portions subsequent to the maxima. The difference is fundamental; and it indicates that the afterglow is chiefly due to some cause other than the recombination of ions, though the period during

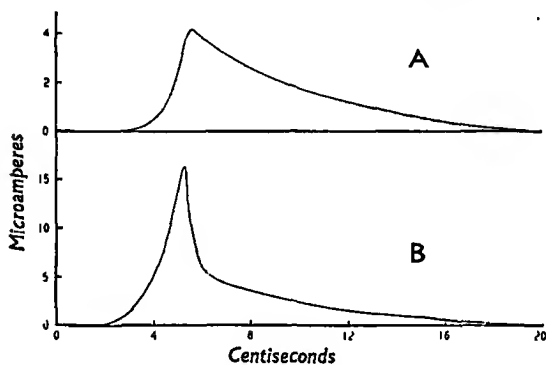


FIG. 15

which this cause operates is closely identified with the period of ionic recombination.

There are also some other more general reasons for believing that the luminosity of gaseous explosions, and notably the afterglow obtained under the experimental conditions described, is principally due to excited molecules formed as a result of the chemical reactions, and not directly to recombination of positive and negative ions. In electric discharges in gases "it is readily shown," say K. T. Compton and Langmuir¹⁵², "that light is principally due, in most cases, to excitation of atoms rather than to recombination of ions". Recombination of ions takes place when a negative and a

positive ion become associated so as to form a neutral system. Such a system may arise from charged ions in several ways. Considering a molecule which has lost an electron and thus become a positive ion, if the negative ions in the system are electrons then a neutral system might be formed in two ways: (1) by the electron colliding with the positive ion, with the simultaneous formation of a neutral normal molecule; (2) by the electron coming within the sphere of influence of the positive ion, and describing a closed orbit of small radius round the positive ion, with the consequent formation of a molecule which is uncharged, but in a state of excitation.

In the first case there will be an emission of energy in the form of radiation. According to J. J. and G. P. Thomson¹⁵³, "neutralisation of positively charged atoms by a negative charge is often the source of luminous radiation, hence it would appear not unlikely that if a large volume of ionised gas were suddenly compressed light would be produced". Newall¹⁵⁴ found that when ionised oxygen was suddenly compressed it became luminous, but Thomson suggests that this cannot be attributed with certainty to recombination.

The amount of energy, however, that is liberated when oppositely charged ions recombine will correspond, unless it takes place in stages, to the ionisation potential of the molecules concerned, say about 12 volts, and this would be responsible for an emission of light in the far ultra-violet, of wave length about 900 Å, and visible light. It is on these grounds that J. J. and G. P. Thomson¹⁵⁵, in Vol. II of their work referred to above, published five years later than Vol. I, have raised a serious objection to the view that luminosity of the gas in electric discharges is due to recombination of negative ions or electrons with positive ions. A similar objection would equally apply in the case of the luminosity of gaseous explosions.

It is, however, possible that the energy change in-

volved during the process of complete recombination, in the formation of a neutral and normal (unexcited) molecule from a positively charged molecule and electron (or negative ion), takes place in at least two stages. The first stage may consist in the formation of a neutral, but excited, molecule in the manner described in (2) above, with the simultaneous emission of radiation. This would correspond to an energy change of a fraction of the ionisation potential, say about 2-3 volts, and would result in emission of visible light. The second stage of the process would consist in the return of excited electrons within the molecule, to lower energy levels, with the emission of radiation in the visible region of a wave length corresponding to each energy level. The ultimate result of this two-stage process would be a neutral and unexcited molecule. At the same time, it seems evident that the more important process in emission of visible radiation is the return of excited electrons to normal levels, within molecules that have been directly excited by chemical and thermal means. Indeed it seems probable that to the operation of temperature on newly formed molecules may be ascribed both the "afterglow" of gaseous explosions and the "aureole" of the separated flame.

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